THE RELATIONSHIP BETWEEN THE COMPRESSIVE STRENGTH OF CEMENT MORTAR AND THE CHEMICAL COMPOSITION AND FINENESS OF CEMENT

A thesis presented as the full requirement for the degree of Master of Science in Engineering at the University of Cape Town, Department of Civil Engineering.

By

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DECLARATION

The writer hereby declares that the work contained herein, with the exception of the quoted sources, is his own and has not been submitted to any other university.

Sean Daron James

Signed by candidate

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ABSTRACT

The purpose of this research was to determine a method whereby predictions of compressive strength could be made with regard to the chemical composition and fineness of Portland cement.

Tests were performed on cement paste and mortar to determine which mixture would yield the most accurate, reproducible results. Paste was found to have a high degree of variation due to its mechanism of failure. Mortar, on the other hand, yielded reproducible and accurate results.

In an attempt to prevent the high variations in the compressive strength of the paste, the paste was evacuated in a special evacuation chamber. The evacuation removed a large volume of air but did not alleviate the variations in the paste strength.

Bleeding was prevented in the paste and mortar samples by rotating the samples during their initial curing period at 3.5 revs/min. A sample of hardened paste, which had been rotated, was scanned through an electron microscope to determine if any visible segregation of the mix had occurred. It was established that no visible segregation was caused to the paste by its rotation during initial setting.

The cement compounds were quantitatively analysed using X-ray diffraction. X-ray diffraction is a direct method of analysing the compounds in cement. Four methods were used to integrate the peak areas and perform background stripping. The cement compounds were then individually compared to the compressive strength of the mortar. The results of the regression analysis showed that an increase in the tricalcium silicate content corresponded to an increase in strength, that dicalcium silicate had little correlation to the compressive strength at 28 days, that a decrease in the amount of tetracalcium aluminoferrite tended to increase the compressive strength and that tricalcium aluminate had little influence on the compressive strength.

The individual regression analyses only gave an indication of the effect each compound had on the compressive strength and could not be used as an accurate indicator because the compounds interact in the cement and do not act individually.

The fineness of the cement was analysed using a laser diffraction spectrometer. The results were expressed as a particle size distribution. The particle size distribution was divided into size bands and compared to the mortar compressive strengths. A regression analysis was performed on the size bands to determine

which bands affected the compressive strength. The results indicated that the particles smaller than 8.48μm and larger than 47.3μm had no significant contribution to the compressive strength at 28 days and that the particles within this size band (8.48μm to 47.3μm) were the only ones which affected the compressive strength.

A multiple regression analysis was used to establish the effect that each of the cement compounds and the fineness of cement have on the compressive strength. Three cases are presented as options for compressive strength prediction of cement mortar. The third case is mathematically the most "economical" model and is expressed as follows :

$$\textbf{28 day Compressive Strength (MPa)} = -7.800 + 0.267(C_3S) + 0.274(\textbf{Fineness})$$

(where "C_3S" represents the % C_3S present in the cement and
"Fineness" the % fines within a specific size range.)

This model relates the cement compounds and the fineness of the cement to the compressive strength. The model has certain limitations, it is only capable of predicting 28 day strengths and since dicalcium silicate has not been taken into account, cognisance will have to be taken of dicalcium silicate if later ages are to be predicted. This means that the coefficients will have to be re-established.

It is recommended that the compounds tetracalcium aluminoferrite and tricalcium aluminate be investigated in greater detail and that the model be adapted for strength predictions at 3, 7 and 28 day ages. It is further recommended that cements with larger compound composition variations be tested and that a method be developed to prevent preferential alignment of the crystals during the X-ray diffraction testing of cement samples.

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GLOSSARY

OPC	- Ordinary Portland Cement
SABS	- South African Bureau of Standards
PCI	- Portland Cement Institute
RMM	- Ready Mix Materials
PPC	- Pretoria Portland Cement
UCT	- University of Cape Town
EMU	- Electron Microscope Unit
SEM	- Scanning Electron Microscope
Micrographs	- Photographs taken at magnification using a SEM.
C_3S	- Tricalcium silicate
C_2S	- Dicalcium silicate
C_3A	- Tricalcium aluminate
C_4AF	- Tetracalcium aluminoferrite
MgO	- Magnesium oxide
CaO	- Free lime (Dead burnt lime)
K_2O, Na_2O	- Alkali oxides
P_2O_5	- Phosphorus pentoxide
$CaSO_4.2H_2O$	- Gypsum
Hydration	- Chemical reaction between cement and water
Clinker	- Material ground, with the addition of gypsum, to make cement.
XRD	- X-ray diffraction
XRF	- X-ray fluorescence
Paste	- A mixture of cement and water
Mortar	- A mixture of cement, water and sand
c/w ratio	- cement to water ratio
SSA	- specific surface area
Flash set	- Immediate stiffening of the paste

CHAPTER 1

INTRODUCTION

The properties of cement are determined first and foremost by its chemical composition and fineness of grinding. The formation of a solid structure from the cement is dependant on the chemical reaction between the constituents of the cement and the water with which it has been mixed. For a given composition, fineness and set of curing conditions, the course of the chemical reaction and therefore the compressive strength is determined by the reactivity of the cement constituents.

This thesis sets out the results of an investigation into the effect that the chemical composition and fineness of Portland cement have on the compressive strength of cement mortar and concrete.

It is known that the chemical composition and fineness of the cement influence the compressive strength although the contribution of each of these factors is unknown.

The cement industry produces cement from raw materials and although they are required to produce a consistent product to within certain chemical composition and fineness parameters, fluctuations often occur beyond the specified tolerances. The fluctuations in the chemical composition, among many other reasons, can have serious implications for the concrete industry as the compressive strength of the concrete is generally considered to represent the "quality" of the concrete. A variation in the chemical compounds and the fineness of the cement may produce concrete with either lower or higher compressive strengths. If the variation results in the concrete having a lower compressive strength than required, then the concrete may be rejected for the purpose it was designed for. Unfortunately, accurate assessment of the compressive strength can only be made a few days after casting the concrete, by which stage the concrete has already set and hardened around the reinforcing and in the shuttering. If the concrete is found to be under the designed strength and is rejected, then the rejected section of the structure must be demolished and be rebuilt or the design of the structure must be modified.

This is especially important to ready mixed concrete manufacturers as the variations due to the chemical composition and fineness of the cement are beyond their control and large claims can be made if the concrete is rejected.

The effect each chemical compound and the fineness of the cement have on the compressive strength should be investigated and analysed so that the fluctuations in the chemical composition and fineness of cement can be catered for in concrete mix design and so that predictions of compressive strength can be made taking

these factors into account.

The objectives of this research were :

1. To determine the effect each major compound has on the compressive strength of concrete.

2. To determine the effect the fineness of cement has on the compressive strength of concrete.

3. To analyse the data accumulated during this research and determine a formula whereby compressive strength predictions can be made using the chemical composition and the fineness of the cement.

The information on which this research is based was gathered by means of a literature review, analysis of cement by X-ray diffraction, electron microscopy, laser diffraction and by casting, curing and crushing mortar samples made with Portland cement of different chemical composition and fineness.

The dissertation begins by describing the materials used and the reasons why certain of the constituents were rejected for this research. It then describes the different mixtures used, the associated problems of bleeding and air entrapment of the mixes and the results of the tests performed on the different mixes.

The methods developed to prevent the bleeding and air entrapment of the mixtures are then described and the results are discussed.

The samples which were subjected to the bleeding prevention method are then analysed to determine whether the method prevented bleeding or promoted segregation. This was accomplished using a scanning electron microscope.

Methods used to cure the samples were upgraded and tested and the accuracy of the compressive testing machine was determined.

The chemical composition of Ordinary Portland cement and the effect that each compound has on the compressive strength is discussed. The methods of analysing the chemical composition are then investigated, comparisons are drawn between two methods and the method chosen for this analysis is described.

The methods used to identify the compounds and the analysis of the results are then discussed. The problem areas in this interpretation and analysis are mentioned and conclusions of the results of the method are drawn.

The effect of the individual chemical compounds on the compressive strength is then examined, each major compound is analysed individually using a regression analysis, the correlation coefficients are compared and the results are discussed.

The effect of the fineness of the cement on the compressive strength is then examined; the tests used to determine the specific surface area and the particle size distribution and the influence fineness has on concrete is then discussed. The method used to grind the clinker to cement and the influence of fineness on bleeding is described. Comparisons are drawn between the percentage particles within a predetermined particle size band and compressive strength.

The results of the fineness and the X-ray diffraction analysis of the cements are converted into percentages of the total amount and the influence of each factor on the compressive strength is determined. The results are analysed and the limitations discussed.

General conclusions are drawn regarding the applicability of the relationship determined between the major chemical composition, the fineness of the cement and the compressive strength.

Finally, recommendations are made regarding the methods used during X-ray diffraction, the calibration of the X-ray diffractometer by testing pure compounds, re-evaluation of the model for early age testing and areas where further investigation of the cement compounds is needed.

CHAPTER 2

MIX MATERIALS

2.1 INTRODUCTION

There are many variables which affect the compressive strength of concrete or mortar. A few of these variables can be controlled and used to manipulate the compressive strength but there are certain factors which are difficult to control and cause fluctuations in strength. Many of these factors influence the water content directly and therefore only have an indirect influence on the strength. These "difficult to control" factors include, among others, the following :

(a) The particle size distribution of the fine aggregate.

(b) The shape, size and texture of the coarse aggregate.

(c) The particle size distribution of the cement.

(d) The chemical composition of the cement.

In order to restrict the number of unknown variables, the materials used in this research have been limited to Klipheuwel sand (fine aggregate) and Ordinary Portland Cement (OPC) from the Pretoria Portland Cement (PPC) factories at De Hoek and Riebeek West. The common coarse aggregate in the Western Cape (Malmesbury Shale) is considered a "poor aggregate" due to its elongated shape and is thus not used in this research, but comparisons can still be drawn between mortar and concrete strengths.

2.2 FINE AGGREGATE

Fine aggregates constitute between 30% and 50% of the bulk mass of concrete and up to 80% of the mass of mortar. Depending on the properties of the concrete or mortar the fine aggregate may have a greater influence than the coarse aggregate.

Fine aggregate can be described as a non-cohesive granular material with the majority of particle sizes between 4.75 mm and 0.060 mm. Particles with grain sizes below this range are classified as silt (60 to 2μm)

or clay ($< 2\mu m$) and are collectively referred to as "dust".

The criteria to be considered in the selection of sand for concrete/mortar are shape, surface texture and the grading of particles, all of which influence the water demand. A good selection of fine material may cause a lower water demand resulting in a higher quality concrete/mortar which exhibits less shrinkage and creep. Good particle shape and grading is very important as a well-shaped sand will result in a low void content in the aggregate system. The grading of the aggregates has no direct effect on the compressive strength but it can have a large influence indirectly for the following two reasons :

1. Poorly graded aggregates result in excessive bleeding and/or segregation which contribute to a reduction in compressive strength.

2. Certain particle sizes tend to entrap small proportions of air. Sands with excessive portions of this particle size will cause an excess of naturally entrapped air to be present in the concrete causing a decrease in the compressive strength.

3. The selection of the aggregate type, grading, surface texture and shape will influence the water requirement of the concrete which ultimately affects the compressive strength.

Segregation has a detrimental effect on the compressive strength of concrete. It is related to most imperfections in concrete such as porous layers, lack of bond and air pockets. It was therefore important to use a well-graded, spherically shaped sand .

For the above reasons Klipheuwel sand was used in all the experimental work instead of the common Cape Flats dune sand. These two sands are briefly discussed below :

2.2.1 KLIPHEUWEL SAND

Klipheuwel sand is considered one of the best sands for making concrete in Southern Africa due to its low water demand, ≈175 l/m^3 of concrete. A grading analysis was conducted and the results obtained, depicted in figure 1, illustrate a grading of this sand.

Although the lower water demand is an economic benefit, this advantage appears to have been offset in Cape Town by the high royalty charged for this sand at the source and the greater costs of transportation. A grading of the Klipheuwel sand used in this research is depicted in figure 1. The envelope has been taken from the suggested outer limits based on the SABS 1083[2.1, 2.2] which is attached in Appendix 11. A sample of the batch used in the experiments was inspected and the

grains were found to have a fairly rounded shape with a rough surface texture.

In order to prevent the segregation of the fine aggregates which were to be used for experimental purposes, the sand was stored in a moist condition in sealed drums and dried at 100 degrees Celsius and allowed to cool for 2 hours before use.

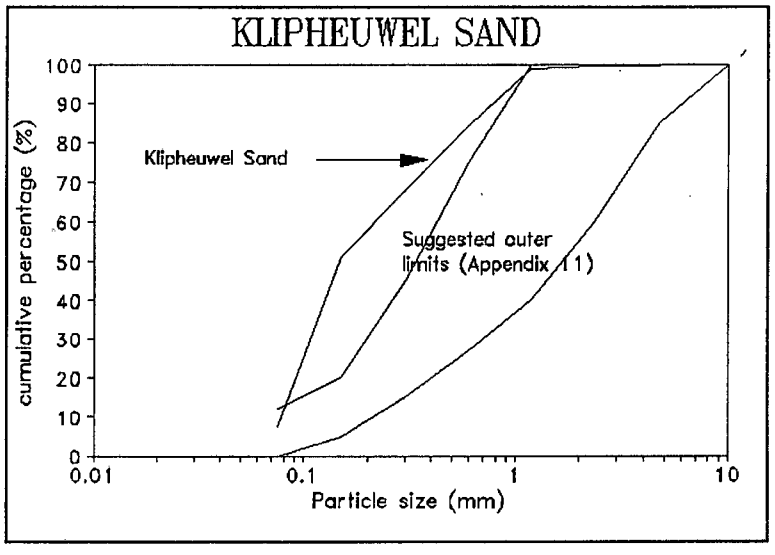

Figure 1 : Typical grading of Klipheuwel sand

2.2.2 CAPE FLATS DUNE SAND

Nearly all the fine aggregate used in concrete manufactured in the Cape Peninsula is Cape Flats dune sand.

A grading analysis conducted on Cape Flats dune sand revealed that its grading extends over about three size fractions only. Approximately 70% of the grains lie between the 1 180 and 150 μm screens. This sand is a "poor" sand as it has few fines. The limited range of sizes and low fines content are responsible for lack of cohesion and promotion of severe bleeding and segregation. The particle size distribution falls outside the recommended limits laid down by SABS 1083[2.1].

Locally, the main source of this sand is near Philippi and west of Mitchells Plain. These sands have had the finer fractions of the sand removed by a process of winnowing and through the action of strong south-easterly winds. Leaching has removed the bulk of the deleterious carbonates in the form of shell fragments. The carbonation of the concrete leads to a lowering of the pH causing the rate of corrosion of the reinforcing to increase rapidly.

Dune sands generally have sizes ranging between 1.00mm and 0.10mm and the Cape Flats dune sands fall in the upper portion of this size range.

Because dune sands are windborne sediments they have well rounded grains. The sorting power of

the wind results in concentrations of material similar in particle size and relative density.

2.3 COARSE AGGREGATE

The influence of the coarse aggregate on concrete strength is difficult to control for the following reasons :

1. The aggregate shape may be flaky or elongated (the length is considered larger than the width, and the width considerably larger than the thickness).

2. The aggregate surface texture may be poor. Surface texture is based on the degree to which the particle surfaces are polished or dull, smooth or rough. These characteristics depend on the hardness and grain size of the parent material.

The full role of shape and texture of aggregate in the development of concrete strength is not known, but possibly, a rougher texture would result in a greater adhesive force between the particles and the cement matrix. According to Kaplan[2.3], surface texture is the most important aggregate property influencing concrete compressive strength. Alexander and Davis[2.4] also propose that texture exercises a profound influence on compressive strength.

Flaky or elongated particles[2.5] (more so than spherical particles) tend to accumulate "bleed water" from the bleeding process beneath them. This causes areas of weakness in the concrete or places where no bond exists. The effect of "bleed water" pockets on strength is difficult to determine as the volume of the pockets is unknown but it will certainly have a negative effect on strength.

It is thus clear that the aggregate qualities have an influence on the compressive strength of concrete but that this influence is difficult to calibrate.

As this thesis is a study of the effect of properties of ordinary Portland cement on compressive strength, no coarse aggregate has been used. It was felt that as the variation in strength due to any one of the chemical compounds in the ordinary Portland cement may be very small, the additional fluctuations in strength caused by the coarse aggregates could mask these variations.

2.4 ORDINARY PORTLAND CEMENT (OPC)

The cement used in this thesis was ordinary Portland cement (OPC) and has been sampled from Pretoria Portland Cement's (PPC) Western Cape plants, De Hoek and Riebeek West.

A composite sample of cement was taken at the de Hoek factory on a daily basis for a period of three months, sealed in plastic containers and delivered weekly to UCT. The sampling and delivery resulted in a delay of one week from manufacture to usage.

The initial investigation on cement paste and cement mortar was performed on cement purchased in 50 kg sacks. This cement was mixed in a drum, sealed in an air tight container and stored in a room which was maintained at a constant temperature.

The bulk of this research was performed on OPC manufactured at the PPC de Hoek plant in the Western Cape but as to show the effect of variation more clearly, samples from another plant (PPC Riebeek Wes) was also tested.

2.5 CONCLUSIONS

From the aforementioned grading analyses and literature review it can be concluded that:

1. The fine and coarse aggregates affect the compressive strength of concrete.

2. Klipheuwel sand is a well graded sand complying with the SABS 1083 recommended grading.

3. Cape Flats Dune sand is a "poor" sand as it has few fines. The lack of fines is responsible for the sand's lack of cohesion, promotion of severe bleeding and segregation.

4. The greywacke or "Malmesbury shale" available in the Western Cape as coarse aggregate are elongated, flaky aggregates. Bleed water accumulates beneath them and affects the overall strength.

5. Because the composite samples of cement, which were tested on a daily basis for three months, were stored in plastic, sealed containers to prevent degradation and tested within a week of sampling the cement can be assumed to be fresh.

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CHAPTER 3

CEMENT PASTE AND MORTAR

3.1 INTRODUCTION

The effect on strength due to the individual chemical compounds may be very small and could be "masked" by variations in the aggregate properties of the concrete. To prevent this masking effect two types of mixtures were investigated. In the first, all the aggregates were eliminated and in the second only the coarse aggregates were left out. The two mixes investigated were thus :

(a) cement paste

(b) cement mortar

The amount of variation each of these mixes had on strength was analysed to determine which mix was more capable of repetitive, consistent results.

Bleeding of the mixes and air entrapment were overcome by developing a method to prevent bleeding and control the degree of air entrapment.

Finally, a curing system was developed and the reliability of the Amsler compressive machine was tested.

3.2 CEMENT PASTE

There is a large number of variables which influence the compressive strength of concrete. Concrete strength is a function of the c/w ratio, the quality of cement and a number of other variables such as the shape, size and surface texture of the fine and coarse aggregates, their gradings and the secondary variables they introduce.

This research was confined to the effect the chemical composition and the fineness of the cement has on compressive strength. A mix comprising only cement and water was used. This mix is commonly known as cement paste.

Alexander[3.1] concluded that tests on cement paste provide a reliable indication of the strength tests of the corresponding concretes. This conclusion was supported by Dalziel[3.2].

3.2.1 BLEEDING AND AIR ENTRAPMENT IN CEMENT MIXES

The use of cement paste presented two major problems. The paste was prone to bleed and secondly, the large proportion of cement in the mix (in comparison to an equivalent mortar or concrete mix) resulted in a very large surface area which caused a high degree of air entrapment to occur. A method was developed to prevent the bleeding of the cement paste and to control the amount of entrapped air.

3.2.1.1 Bleeding

Bleeding occurs when the solid particles settle in the mix. This settlement or sedimentation continues until sufficient stiffening of the cement paste has occurred to prevent further occurrence of this process. The settlement is due to the slight separation of the adjacent particles at the points of near contact which enables the particles in freshly mixed paste to settle through the fluid in which they are suspended[3.3]. The settlement is activated by the force of gravity and operates because of the difference in the specific gravity of the two constituents in the cement paste, namely cement ($3.14kg/m^3$) and water ($1.00kg/m^3$). Since the particles near the bottom can settle in a shorter length of time than those at the top, the sedimentation increases the density at the bottom of the sample relative to the top. When the cement particles settle, they displace the water particles which eventually find their way to the surface of the mix where they form a layer of clear water. The degree of water formation on the surface is only an indication that bleeding has or is occurring and is not directly related to the bleeding capacity of the mortar or concrete.

The bleeding process forms capillaries which form a continuous inter-connected system. The degree of microscopic capillary formation would be aggravated by a low c/w ratio. The capillaries are sufficiently large enough that the hydration process of the cement cannot block or close them off[3.3]. Consequently, it can be assumed that the bleeding of a mix would influence the strength, as well as produce a more porous paste with a changed c/w ratio, a variable size (as the bleed water eventually evaporates) and a sample with a varying density.

Since bleeding can affect the compressive strength results of a series of tests the variability

should be prevented.

A system was developed to spin the cubes at a specific rate to prevent the sedimentation of the particles and thus prevent bleeding. The standard cube moulds, which were old and slightly damaged, had to be modified such that they were water tight and square. They also had to have lids attached.

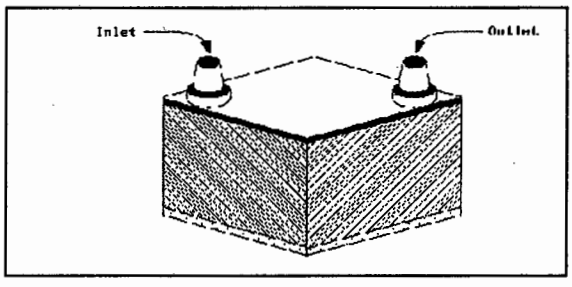

Figure 2 : Typical cube mould

The moulds (Figure 2 and Appendix 10) were manufactured in the workshop of the Department of Civil Engineering at the University of Cape Town and enabled the cubes of cement paste and mortar to be spun, thereby preventing the mixes from bleeding . The moulds were machined to accurate specifications to ensure that they were water tight. Lids with an inlet and outlet were fitted to the cubes to allow access for the paste and an outlet for the air.

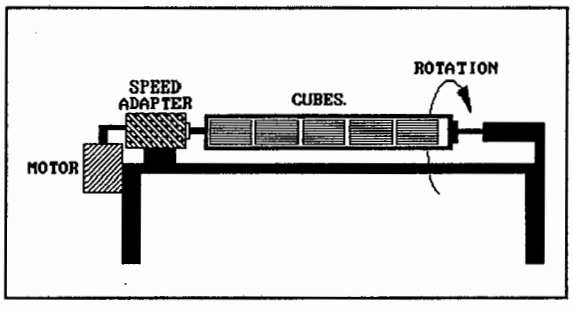

Figure 3 : Bleeding rotation apparatus

A second machine, also produced in the above workshop, was made to rotate the moulds at a rate of 3.5 revolutions per minute (Figure 3 and Appendix 10).

A c/w ratio of 0.33 was used for the cement paste. This is a non-viscous mix and was chosen because it had to flow from the evacuation cylinder into the cube.

Cubes taken from the bleeding prevention apparatus were analysed using an electron microscope to determine whether sedimentation in any form or segregation had occurred. The rate of rotation may have created sufficient centrifugal forces within the cube to cause segregation of the mix. The results of the electron microscope analysis indicated that no segregation or sedimentation had occurred.

3.2.1.2 Entrapped Air

An increase in the entrapped air in a mix can result in a considerable reduction in the compressive strength of cement paste, mortar or concrete. Cement paste is known to contain numerous discontinuities such as pores, fissures and voids which lead to high stress concentrations in the material under load. A very high stress is reached in small volumes of the specimen resulting in microscopic fracture[3.4]. The presence of voids in concrete can reduce the strength by 6% for every 1% of air such that a 5% air content (by volume) of concrete will result in a 30% reduction in strength[3.5]. Concrete entraps between 1 and 2.5% air and mortar entraps approximately 8%[3.5]. If the relationship between the amount of cement in the mix and the percentage air entrapped is linear then the air entrapment of paste should be greater than 20%. The proposed air entrapment in cement paste cannot be substantiated by work conducted during this research and would be very difficult to quantify as mixtures and mix constituents vary. It is the authors opinion that this estimate, when compared to that for mortar and concrete, puts cement paste in perspective when comparing the affects of air entrapment on compressive strength. The variations in strength due to this amount of air entrapped in the mix would not justify research on paste unless the entrapped air content could be reduced. The amount of air in a mix is thus critical and must be controlled.

Cement paste entraps more air than concrete (for the same cement/water ratio) because the surface area in cement paste far exceeds that of concrete. It was therefore necessary to remove as much entrapped air as possible.

In an attempt to produce a cement paste with a reduced percentage entrapped air the cement paste was subjected to a partial vacuum, after mixing and prior to casting, for a period of 15 minutes.

The apparatus used to de-air the cement paste (Figure 4) involved a cylinder with a tapering base to which an air tight valve was attached. The top of the cylinder was connected to a vacuum pump. Vacuum pressure was applied which caused the cement paste to "bubble" and large amounts of air were expelled. The degassing process was limited to 15 minutes as the rate of "bubbling" had decreased significantly. Segregation did not occur during this period due to the continuous mixing of the paste by the rising air bubbles.

The vacuum applied to the cement paste was not sufficient to remove mix water in the

form of vapour. This was proven by de-airing a sample of water for two hours. The weight of the sample prior to degassing and after the test did not differ.

After degassing of the cement paste was complete the outlet valve was opened and the paste flowed into the cube moulds. The cubes were vibrated to remove any large air pockets entrapped during casting and were then loaded into the bleeding rotation machine (Figure 3).

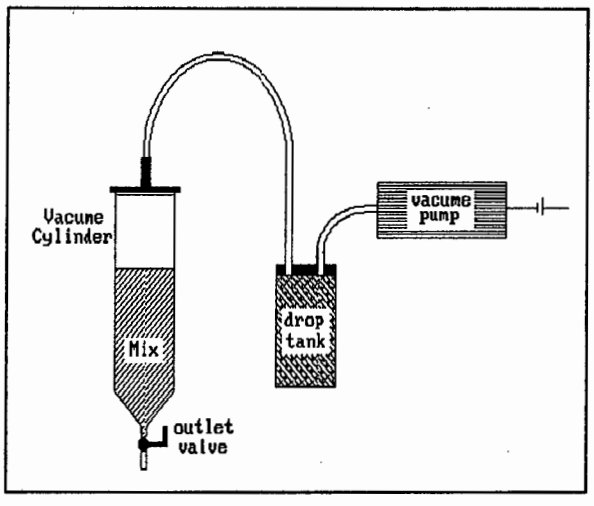

Figure 4 : Cement paste evacuation apparatus

3.2.2 MIX PROPORTIONS, PROCEDURE AND CASTING

A c/w ratio of 0.33 was used for cement paste and as it was necessary that the mix be fluid enough to flow through narrow diameter tubing under its own weight. In choosing the c/w ratio for the cement paste no consideration was given to firstly, a specific range of compressive strengths and secondly, that the high amount of water would result in an increase in the amount of unbonded water. The unbonded water in the form of voids or capillaries, which are the residue of the original water filled spaces in the fresh paste, can affect the compressive strength.

A c/w ratio of 1.54 (Table 2) was used for cement mortar. This mix was stiffer than the paste mix but was sufficiently fluid enough to pass through the evacuation apparatus and into the cube moulds. Cement can achieve total hydration only if the original water/cement ratio is greater than 0,38 by mass. For ratios below this value the paste will always contain unhydrated cement while for ratios in excess of this value the paste will always contain some space not filled by gel, that is capillary pores[3.3].

The cement was placed in a Hobart variable speed mixer and water was added slowly over a period of one minute until a consistent paste was formed. The paste was then mixed at a high speed for a further minute and cast, through the intricate system mentioned above, into standard 100mm x 100mm cubes. The cubes were then vibrated on a vibration table for 1 minute, sealed and loaded onto the bleeding rotation apparatus in a temperature controlled room.

The cement paste tended to bleed badly due to the low c/w ratio. The low c/w ratio resulted in a "wet" mix with a higher rate of sedimentation than that for a mix with a higher c/w ratio. The bleeding had to be prevented as the degree of bleeding could not be accurately determined. The change in the c/w ratio due to the bleeding would have an influence on the compressive strength of the sample, therefore the bleeding of the paste had to be prevented before the test could be used as an accurate indicator of the compressive strength.

3.2.3 CEMENT PASTE RESULTS

The cement paste cubes (which were all cast from the same batch of cement) were stripped after one day and cured in a lime saturated water bath at a constant temperature of 25 degrees celsius. At 28 days curing the cubes were crushed in accordance with the SABS Method 863 [3.6]. The results are listed in Table 1 below :

TABLE 1 : COMPRESSIVE STRENGTH OF PASTE MIXES

TEST NO.	CUBE 1 (MPa)	CUBE 2 (MPa)	CUBE 3 (MPa)	AVE (MPa)	STANDARD DEVIATION (MPa)	COEFFICIENT OF VARIATION (MPa)
1	67.0	46.0	73.5	62.17	1.50	2.19
2	58.2	62.3	59.5	60.00	2.01	2.93
3	70.0	67.6	69.5	69.00	0.11	0.16
4	75.9	66.6	73.6	72.03	0.83	1.21
5	71.7	68.0	72.1	70.60	0.49	0.72
6	78.3	69.0	67.3	71.53	0.71	1.04
7	58.3	65.5	70.0	64.60	0.92	1.34
8	61.3	60.4	65.0	62.23	1.48	2.16
9	75.9	66.7	77.2	73.27	1.12	1.63
10	75.4	76.1	76.3	75.93	1.75	2.55
11	73.8	77.5	66.0	72.43	0.92	1.34
12	73.4	77.5	66.0	72.30	0.89	1.30
13	71.1	63.0	71.4	68.50	0.01	0.01
14	74.1	79.3	69.3	74.23	1.35	1.97
15	67.3	73.8	68.3	69.80	0.30	0.44
16	43.6	63.6	62.0	56.40	2.86	4.17
17	46.3	65.0	77.8	63.03	1.29	1.88
18	63.3	73.7	75.1	70.70	0.51	0.74
19	62.5	77.8	79.2	73.17	1.10	1.61

* Note : Standard deviation cannot strictly be applied to a set of three tests however, in this research it was deemed necessary to use the "Standard Deviation" to clarify a point.

The compressive strength results of the cement paste tests in Table 1 above are very high but given the curing methods of evacuation, rotation and under water constant temperature curing, these results represent a paste with far less flaws than normal cement paste. The above results of the cement paste cubes are therefore justifiable.

The "standard deviation" of a set of cubes varies from 12.07 to 0.37 MPa. The "standard deviation" of the averages of each set are 4.46 MPa. The coefficient of variation in a set of cubes ranges from 18.39% to 0.49%. Considering that all the results in Table 1 relate to a single sample of cement, the variation in the compressive strength are rather high. It is therefore not possible to compare the compressive strength results of cement paste and the chemical composition or the fineness of the cement because the inherent variations in the paste are too high.

The reasons for the failure of the cement paste method of analysis may be due to :

(a) The low c/w ratio and thus the high water content cause a large amount of unbonded water to remain in the hardened cement paste. The unbonded water acts as voids which influence the compressive strength.

(b) The amount of air entrapped in the mix affected the compressive strength as the air bubbles act as voids. Cement paste entraps a large amount of air in comparison to concrete or mortar because paste has a higher surface area.

(c) The failure mode of cement paste.

The failure mode of cement paste is explosive. This is due to the fracture mechanism of paste. When a micro-crack forms, its propagation is not blocked by the surrounding material and the cube fails. If the strength of a specimen is governed by the weakest element in it, the problem becomes that of the proverbial weakest link in a chain. Thus, any weakness in the cement paste would tend to aid the propagation of micro-cracks. In concrete and mortar, the propagation of the micro-cracks are halted or slowed down by the aggregate (fine or coarse) as the crack either has to pass through or go around the aggregate. This is confirmed since neither low-strength mortar nor concrete fails explosively when tested in a very stiff machine. Mortar was chosen above concrete for further research since mortar has fewer variables than concrete.

3.3 CEMENT MORTAR

Mortar is a mix of sand, cement and water. The reason for introducing sand into the mix was to prevent

the propagation of micro-cracks and the explosive failure mode found to occur in the cement paste.

A sand with smooth, rounded particles and a good particle size distribution has the best workability. Of the sand available in the Western Cape with these characteristics, Klipheuwel sand was used.

The constituents of the mortar were mixed in the following ratio :

TABLE 2

CEMENT	SAND	WATER
1	2.5	0.65

* Measured by mass

The above proportions produced a non-viscous mortar capable of being cast from the vacuum cylinder into the cubes. The mortar was mixed in the following orderly manner to ensure that a consistent mixture was obtained :

(a) Firstly, the sand and cement were mixed together

(b) Water was then added to the cement/sand mixture at a slow mixing rate over a period of one minute. The paddle rotation during slow rotation was 24 revs/min.

(c) Finally, the mortar was mixed at a high shear rate to promote thorough mixing. The paddle rotation during high shear was 120 revs/min.

The mortar was then fed into the cubes which were vibrated at an angle of 45 degrees for 1 minute to remove all the air. The cubes were sealed, spun and stripped the following day. They were cured in a lime saturated, temperature controlled water bath for 28 days. The mortar was not evacuated as this led to severe segregation of the mix in the evacuation cylinder. The cubes were crushed with the faces, which formed right angles to the direction of rotation on the bleeding apparatus, being the faces which made contact with the upper and lower crushing platens. The initial work on mortar (results in Table 3) was used to analyse the consistency of the test method and was not used in later regression analyses.

3.4 CEMENT MORTAR RESULTS

To determine if mortar cubes could be used as a standard test for further investigations, 17 sets of cubes were cast in batches of three using the same batch of cement and sand for all the tests. The results of these tests showed a great improvement on the paste results. The cement mortar was not subjected to the evacuation process developed for the cement paste as it caused the mortar to segregate. The average standard deviation for all the mortar cubes was 0.29 MPa. The results of the mortar tests can be seen below in Table 3.

TABLE 3 : COMPRESSIVE STRENGTH OF MORTAR MIXES

TEST NO.	CUBE 1 (MPa)	CUBE 2 (MPa)	CUBE 3 (MPa)	AVE. (MPa)	STANDARD DEVIATION (MPa)	COEFFICIENT OF VARIATION (MPa)
1	26.2	26.1	**29.8**	27.37	1.39	5.47
2	24.4	25.9	26.0	25.43	0.02	0.08
3	25.7	24.3	24.6	24.87	0.37	1.46
4	24.4	24.1	25.6	24.70	0.49	1.93
5	24.6	24.7	25.1	24.80	0.42	1.65
6	26.3	24.7	25.8	25.75	0.25	0.98
7	26.1	24.9	26.2	25.73	0.23	0.91
8	24.9	24.3	26.0	25.07	0.23	0.91
9	25.7	26.2	24.5	25.47	0.05	0.20
10	25.9	25.8	25.2	25.63	0.23	0.91
11	26.4	25.5	24.0	25.30	0.07	0.28
12	26.2	26.1	24.3	25.63	0.16	0.63
13	28.8	24.5	26.3	26.53	0.16	0.63
14	25.7	24.3	24.1	24.70	0.49	1.93
15	24.9	27.8	24.1	25.60	0.14	0.55
16	25.1	24.0	26.0	25.03	0.26	1.02
17	25.1	25.2	26.1	25.47	0.05	0.20

* Note :

1. The figures in bold represent "outliers"
2. The standard deviation in this table is not strictly correct as only three samples have been used to determine the mean. The "standard deviation" above has simply been used to illustrate a point.

The coefficient of variation is 2.86% and ranges between 0.14% and 6.09%. The standard deviation varies from 0.04 MPa to 1.61 MPa. The improvement in the variability of the compressive strength results for the mortar indicated that the failure mode of the paste was due to the lack of aggregates which would have

impeded the micro-crack propagation. The results in Table 3 showed that cement mortar, as opposed to cement paste, was a reliable indicator of compressive strength and that repeatable work could be performed.

3.5 CURING OF MORTAR AND PASTE SAMPLES

The type of curing a hydraulic cement experiences can influence its final engineering properties, for example, the strength of concrete/mortar depends on, amongst other factors, the temperature and moisture content during curing and the age of the sample at testing.

Therefore, the factors controlled during the curing process were the moisture content, temperature and the age of the sample. The mortar samples were rotated in the same cube moulds as those used for the paste cubes, the only difference being that the mortar samples were not evacuated in the vacuum cylinder. The vacuum cylinder was only used to pour the mortar into the cube moulds. If the specimen is allowed to dry out, hydration will terminate and no further strength will develop unless moisture can again penetrate the sample. Temperature will affect hydration and extreme temperatures, (-12°C and below) will prevent further hydration. The age of the specimen is important as the degree of hydration is proportional to time. An increase in the curing period will result in an increase in strength.

Curing not only influences the strength but good curing will also reduce permeability and increase durability.

The specimens were cured under water at a constant temperature for exactly 27 days, thereby eliminating all the variables in concrete curing.

To create effective curing conditions the curing tanks were covered and lined on the outside with polystyrene boards. These were used to insulate the tanks against air temperature change. To prevent a change in temperature due to seasonal change a thermoregulator was installed at each end of the tanks. The thermoregulators maintained the water temperature at 25°C with a maximum fluctuation of 0.5°C either way.

The cubes were all cured like this for 27 days and then tested.

3.6 COMPRESSIVE STRENGTH

The compressive strength of concrete is considered its most important engineering characteristic. Other characteristics such as tensile strength, elastic modulus, shrinkage, creep, impermeability and durability are also important, however, the compressive strength is the most commonly used single characteristic for the measurement of the "quality" of concrete.

The compressive strength test on a cube is only representative of the strength of that shape of specimen tested for particular conditions of manufacture, curing and testing. As a result, all the specimens tested in this research have been tested according to SABS Method 863.

3.6.1 THE ACCURACY OF THE AMSLER COMPRESSIVE STRENGTH TESTING MACHINE

A batch of cement paste was specifically made in order to check the consistency of the batching, mixing, casting, curing and crushing procedures. The results of the compressive tests on the cement paste (Table 1) indicated that there was a severe problem which amongst others could be due to the compressive testing machine.

A series of comparative tests on 150mm X 150mm X 150mm concrete cubes, cured and crushed in accordance with the SABS Method 863[3.4], was run by Ready Mix Materials (RMM) and involved four participating parties, namely :

1. Ready Mix Materials (RMM)

2. Portland Cement Institute (PCI)

3. South African Bureau of Standards (SABS)

4. University of Cape Town (UCT)

The concrete cubes were all made and cured by RMM and then delivered to the parties on the day of testing. The results of these tests showed that the compressive testing machine used for this research was not at fault (regarding the variations in cement paste) and that the error lay elsewhere. Table 4 shows a set of results of the compressive strength of UCT's samples in comparison to the other participants. A copy of the results is attached in Appendix 1. The results of the tests below show a 2.0 MPa or 4% variation in the UCT results. According to BS 1881 : Part 115 : 1986[3.7] this accuracy is not sufficient but as the other participants; RMM (3.51%), PCI (2.3%) and SABS (8.3%) all had similar or worse accuracies, the UCT compressive machine was acceptable.

TABLE 4 : COMPARATIVE TESTING - AMSLER COMPRESSIVE MACHINE

CUBE NO.	RMM (MPa)	PCI (MPa)	UCT (MPa)	SABS (MPa)
4850 A	44.5	42.5	44.5	46.0
4850 B	44.5	43.0	46.0	48.0
4850 C	39.5	43.5	46.5	50.0
AVERAGE	43.0	43.0	45.5	48.0

3.6.2 THE COMPRESSIVE STRENGTH TEST

The compressive strength test was performed according to SABS Method 863[3.4]. Before any crushing was done, the machine bearing surfaces were wiped clean and any dirt or grease was removed from the surfaces of the cube. The cube was centred on the lower platen of the Amsler compressive machine in order that the load was applied to the side faces of the cube as cast. The load was applied at a steady rate of 15MPa/min until the cube failed. As the Amsler machine (Appendix 9) is a manually operated machine, care was taken to maintain the loading rate constant as cube failure approached.

The maximum load applied was recorded for each cube and the compressive strength of the cube was calculated by dividing this compressive load by the cross-sectional area of the cube.

3.7 CONCLUSIONS

In order to detect the effect on compressive strength due to small changes in the chemical composition or the fineness of the cement it was necessary to develop a suitable method of test with limited variables. The method should yield consistent, repeatable results. It can be concluded from the results presented that :

1. Cement paste : Cement paste was not suitable for consistent, repetitive work because it's explosive mode of failure resulted in erratic, inconsistent data, presence of voids, bleeding, segregation, etc.

   The cement paste entrapped a high degree of air because the total surface area of the cement paste, in comparison to a concrete mix of the same cement/water ratio, was high.

2. Cement mortar : The results performed on cement mortar showed that this mix was suitable for consistent work. The explosive mode of failure was prevented by the addition of fine aggregate. Cement mortar can thus be used for further analysis.

3. Curing : The modified curing tanks prevented temperature changes during the curing period.

4. Compressive strength : The Amsler compressive strength testing machine was assessed in comparison to three other individual testing machines. The Amsler was found to be

accurate for the purposes of the tests to be conducted.

5. Bleeding : Bleeding causes sub-microscopic "bleed" capillaries which affect compressive strength. Bleeding was overcome by spinning specially manufactured cubes at 3.5 revolutions per minute.

6. Air content : Cement paste was evacuated to remove entrapped air. This method effectively removed air from the cement paste but was not suitable for cement mortar as it caused the mortar to segregate.

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CHAPTER 4

MICROSCOPIC ANALYSIS OF CEMENT PASTE

4.1 INTRODUCTION

During the initial setting period of the cement paste cubes they exhibited pronounced bleeding tendencies. The bleeding caused a change in the effective cement/water ratio, was responsible for the formation of capillaries[4.1], and caused the cubes to vary in size. These variations all influenced the ultimate compressive strength. The bleeding of the cement paste cubes thus had to be prevented and was accomplished by rotating the cement paste cubes until the (initial) set had taken place. The rotating process is dealt with in greater detail in chapter 3.

The rotation of the cubes resulted in small centrifugal forces being set up within the cube sample. The initial test work was performed on a machine which rotated at 22.3 revs/min and the microscopic analysis was performed on these cubes. An improved rotating machine (3.5 rev/min) was used for work performed at a later stage. A major concern was that the centrifugal forces would cause segregation of the mix according to density and would result in a cross-section of the cube showing a variation ranging from high density at the exterior to a low density at the centre of the cube. Low density conditions are identified by an accumulation of air bubbles (for example) and can be observed using an electron microscope.

If the forces within the cube due to rotation were large enough and caused a variation in density then the compressive strength would result in a lower cube compressive strength.

A "Cambridge S200" scanning electron microscope was used to check for any significant variation in the visible density of the cubes and to view the detailed surface structure of the specimens. Secondary electron micrographs were recorded at 10KV between 100 and 250 magnification and the samples were mounted at a 35 degree tilt. Images were obtained when the primary electrons interacted with the sample and produced secondary electrons, which in turn were detected and displayed on a screen.

4.2 PREPARATION OF THE SAMPLE

4.2.1 SELECTION AND EXTRACTION OF THE SAMPLE

In order to obtain the maximum deviation in the density of the sample (should a deviation occur) due to the centrifugal force, it was necessary to extract the sample from the part of the cube that had the centre of rotation passing through it at right angles to the axis of rotation (Figure 5).

The sample was cut using a diamond tipped blade, notched at equal distances and sheared. The sample was sheared by applying a point load opposite the notch so that a natural surface could be examined under the scanning electron microscope (Figure 6).

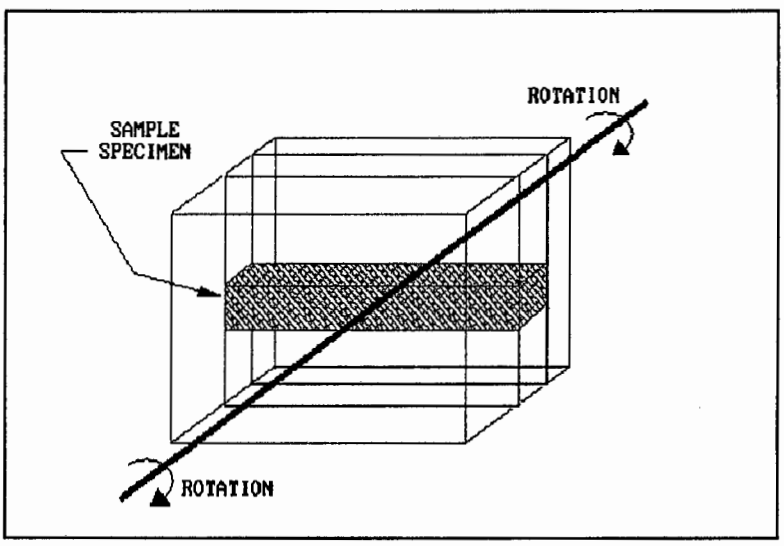

Figure 5 : Mortar specimen selection

4.2.2 SURFACE PREPARATION

All extraneous contaminants were removed from the specimens (oils from human contact, dirt and dust) using a solvent. The specimens were then air dried. The removal of the contaminants was necessary to obtain a precise secondary electron image.

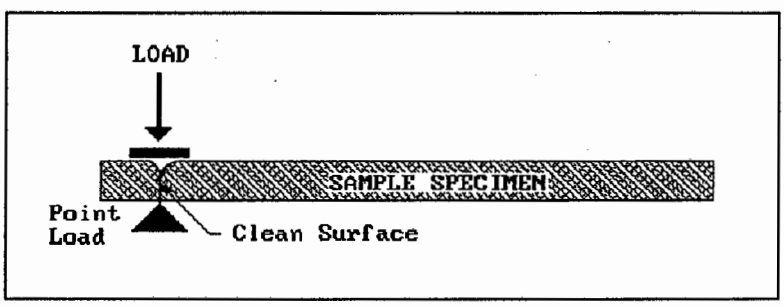

Figure 6 : Shearing of the sample to expose the natural surface

4.2.3 MOUNTING

The specimen was mounted on a "Cambridge" 100 stub. The specimen was securely attached to the stub so that during manipulations within the specimen chamber it would not fall off. The specimen

was attached using a 50/50 mixture of acrylic alcolex glue and a colloidal graphite mix. The stub was made out of a conductive material (polished aluminium) so that it could conduct current produced by the electron beam away from the specimen. The specimen had to be in close, tight contact with the stub. It could not extend over the side of the stub surface any more than necessary as insufficient contact would result in a charge build up on the specimen which would cause distortion of the image. This charge build up is known as charging.

4.2.4 DEHYDRATION

Most specimens of paste and mortar contain a certain amount of moisture. Wet specimens are difficult to examine under the electron scanning microscope at temperatures above freezing. The suction force in the evacuated column causes water loss to any non-dehydrated sample. The water loss from the specimen can result in contamination of the column as well as damage to the topography of the sample[4.2]. As the water rapidly evaporates, the wet specimen is subjected to air drying and freezing which would cause damage to the frozen, unbonded water in the mix. The samples were therefore dehydrated prior to testing.

The temperature and pressure was varied in a special chamber until the liquids changed from a liquid phase to a gaseous phase. The temperature and pressure at which this change from one phase to another occurred is called the "critical point"[4.3]. A problem associated with this form of dehydration is that the surface of the sample can become slightly rearranged, causing cracks throughout the sample. These shrinkage effects are visible on the micrographs in Appendix 2.

The samples which had not been dehydrated did not appear to have the micro-cracks apparent in the dehydrated samples. This was tested by using simple optical magnification and not the electron microscope as the undehydrated sample could damage the SEM, as mentioned earlier. For this reason comparative micrographs are not available. This indicates that the micro-cracking visible on the micrographs was due to the dehydration process.

4.2.5 COATING OF THE NON-CONDUCTIVE SAMPLE

Cement paste is not a good conductor of electricity. The mortar was made conductive by coating the specimen with a thin layer of conductive material. This was done by sputter coating the sample with 20 nanometres of gold palladium. Gold palladium is a compressed metal comprising a mixture of the elements gold and palladium. Both the elements exist on the periodic table where gold has an atomic number of 79 and palladium, 46.

If the specimen did not have a conductive coating then "charging" would occur as a result of the insulated surface being subjected to the electron beam. The electron beam imparts a negative charge to the surface of the sample and without the conductive coating the charge cannot be dissipated.

The conductive coating connects the non-conductive specimen surface to a grounded stage preventing a negative charge build up on the surface of the specimen.

4.3 TESTING DETAILS

Ten samples were tested on the Cambridge S200 scanning electron microscope at the Electron Microscope Unit (EMU) at UCT. A diagrammatical representation of the EMU can be seen in Figure 7. Secondary electron images were attained at 10kV and micrographs were recorded at both 100 and 250 magnification. The samples, mounted on stubs , were placed on a moveable clasp within the specimen chamber at a tilt of 35 degrees.

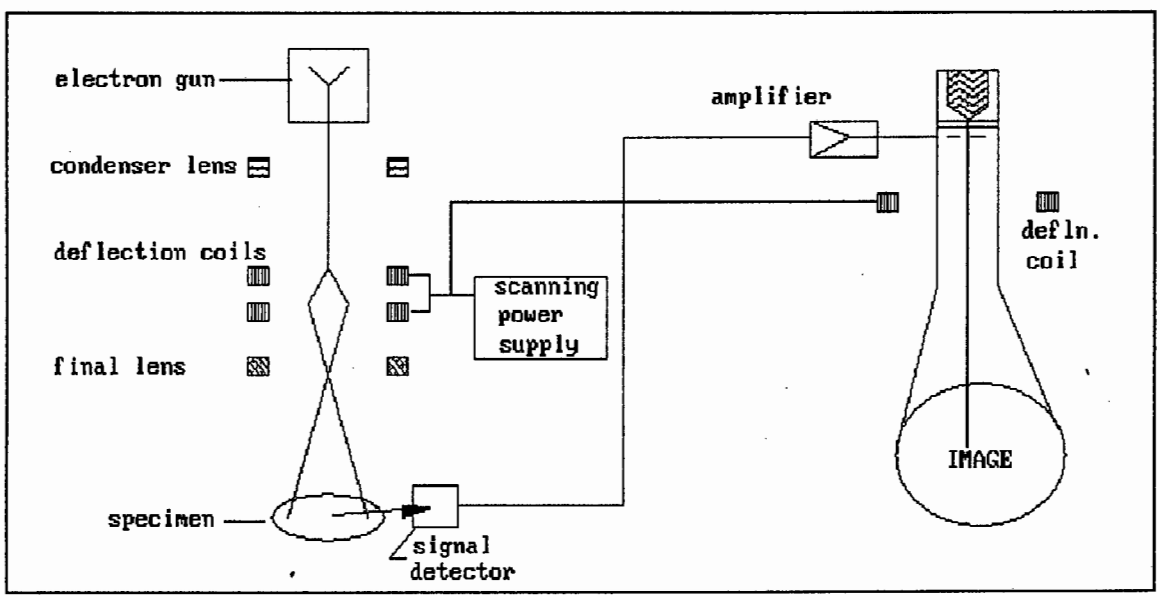

Figure 7 : SEM image projection[4.4]

4.4 RESULTS

The micrographs produced from the testing of the sample (Appendix 2) indicated that there was no significant variation in the micro-structure of the sample. By observing a range of micrographs whose

location within the cube varied from the outside of the cube to the centre, it was noted that there was no apparent concentration of bubbles (a more porous microstructure - see Appendix 2) which would indicate a lower density.

The air bubbles in the micrographs should not be confused with the larger dark spaces caused by shadowing. Shadowing occurs when the beam from the electron microscope does not impinge on the whole surface area of the specimen because of the rough topography of the surface (Figure 8).

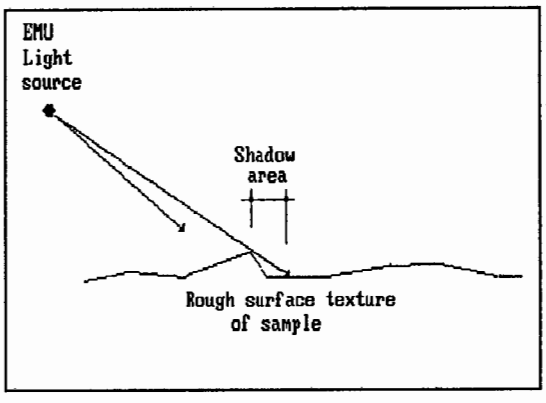

Figure 8 : Shadowing of the EMU light

The micrographs recorded at 100 times magnification, clearly showed a consistent surface texture which confirmed that there was no variation in density. The micrographs which were recorded at 250 times magnification clearly indicated the air voids. These micrographs also confirmed that there was a uniform pattern of air pockets throughout the cube.

4.5 CONCLUSIONS

The micrographs recorded at various magnifications by the scanning electron microscope have shown that there is an even distribution of air bubbles or porous microstructure throughout the sample. This shows that there is no significant variation of apparent density within the sample.

Since the micro-cracks observed on the micrographs appear to have been caused by the dehydration process during preparation for the scanning electron micrograph one can conclude that they are not due to the effect of the centrifugal forces caused during the bleeding prevention process.

Therefore, it can be concluded that no damage, or segregation, was caused inside the cubes by their rotation at 22.3 rev/min. It is thus safe to assume that the cubes used for the main body of the research which were rotated at 3.5 rev/min were not subjected to centrifugal forces capable of affecting their densities.

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CHAPTER 5

THE CHEMICAL COMPOSITION OF ORDINARY PORTLAND CEMENT

5.1 INTRODUCTION

According to BS 12[5.1], Portland cement is a cementitious material which is obtained by :

> *"intimately mixing together calcareous or other lime bearing materials with, if required, argillaceous and/or other silica, alumina, or iron oxide bearing materials, burning them at a clinkering temperature and grinding the resulting clinker."*

Cement is a heterogeneous substance made up of several fine grained minerals which are formed during the clinkering phase. It is therefore difficult to get a perfectly consistent product due to the impurities and changing composition of the raw feed.

Portland cement consists of four main crystalline compounds (also called phases) made up of calcium oxide (CaO), Silica (SiO_2), Alumina (Al_2O_3), and iron oxide (Fe_2O_3). In cement chemistry it is usual to describe each oxide by a single letter, namely :

TABLE 5 : OXIDE ABBREVIATION

OXIDE	OXIDE ABBREVIATION
CaO	C
SiO_2	S
Al_2O_3	A
Fe_2O_3	F
H_2O	H

During the clinkering phase the oxides bond to form tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium alumino ferrite. Accordingly, each compound is written as follows :

TABLE 6 : COMPOUND ABBREVIATION OF CLINKER PHASE

ABBREVIATION	COMPOUND
C_3S	TRICALCIUM SILICATE
C_2S	DICALCIUM SILICATE
C_3A	TRICALCIUM ALUMINATE
C_4AF	TETRACALCIUM ALUMINOFERRITE

The chemical compounds are also referred to by their full chemical definitions or common chemical name :

TABLE 7 : CHEMICAL DEFINITION

ABBREVIATION	COMMON CHEMICAL NAME	CHEMICAL DEFINITION
C_3S	Alite	$3CaO.SiO_2$
C_2S	Belite	$2CaO.SiO_2$
C_3A	Celite	$3CaO.Al_2O_3$
C_4AF	Felite	$4CaO.Al_2O_3.Fe_2O_3$

The amount of each compound formed can be influenced by the conditions the clinker is exposed to during and after formation such as reducing conditions and the clinker cooling stage.

The effect of reducing conditions in the burning zone is a change of Fe_2O_3 to FeO[5.2]. In this case the quantity of C_4AF in the melt is reduced resulting in an increased C_3A content since more Al_2O_3 is available to react with lime to form C_3A[5.2]. The effect of the increased C_3A content is to shorten the cement setting times dramatically.

After leaving the burning zone, the clinker is cooled at a controlled rate to maintain as much C_3S content as possible. Slow cooling leads to a reaction between the liquid phase and the C_3S resulting in the formation of more C_2S and C_3A. However, slow cooling may also cause "dusting" which is the inversion of C_2S to the C_2S gamma form[5.3]. C_3S is unstable at temperatures below 1250 degrees celsius and degrades into C_2S. The rate of cooling must therefore be such to prevent this degradation. It is clear that the percentage of

each compound will vary according to the process of clinker manufacture.

Cement is a heterogeneous material made up of several fine grained materials which are formed during the clinkering process. The cement clinker has four minerals, namely, alite, belite, felite, and celite. These are essentially the same as tricalcium silicate (alite), dicalcium silicate (belite and felite) and tetracalcium aluminoferrite (celite).

The combined content of these compounds is approximately 90% of the cement weight which is why they are referred to as the major compounds.

None of the major compounds exist in pure form, and all four contain small amounts of other oxides in solution. The presence of such substitution affect the properties of the compounds and causes the predicted compound composition to vary from the "true" one. These impurities are referred to as the "minor constituents".

The more important of these minor constituents are magnesia, alkali oxides, phosphorus pentoxide, free lime and sulphates. These can cause variations in strength and durability of hydrated cement which may be out of proportion to the percentage present.

The chemical composition controls the rate of development of the heat of hydration. Typical values of the heat of hydration of pure compounds are :

TABLE 8 : COMPOUND HEAT OF HYDRATION

COMPOUND	HEAT OF HYDRATION (J/g)
C_3S	502
C_2S	260
C_3A	867
C_4AF	419

The heat of hydration is dependant on the chemical composition, but there is no relationship between the heat of hydration and the cementing properties of the individual compounds. Also, because the rate of hydration differs for the various phases, the rate of heat evolution is not constant with time.

The two silicates primarily responsible for the strength of hydrating cement pastes are tricalcium silicate

(C_3S) and dicalcium silicate (C_2S). C_3S contributes most to the strength gain during the early stages (up to 28 days) and C_2S influences the gain in strength mostly from 28 days on. After a period of approximately one year, the two compounds have contributed (for the same weight) about the same to the ultimate strength. The rate of strength development for the individual compounds is shown diagrammatically in Figure 9.

The graph in Figure 9 represents the strength development of neat pastes and cannot be strictly interpreted as occurring in this manner in cement paste, mortar or concrete. This is because the compounds all interact in the cement paste, mortar and concrete and do not act individually as "neat" compounds.

Tricalcium Aluminate (C_3A) has a controversial role. It is claimed C_3A affects the rate of strength gain of C_3S. It is also claimed that C_3A contributes to the strength of the hydrating cement paste for the first one to three days. The effect of tricalcium aluminate on hydrating cement paste has been less clearly established[5.4].

Tetracalcium Aluminoferrite (C_4AF) has no known positive contribution to the strength of hardened cement paste[5.2, 5.5, 5.6].

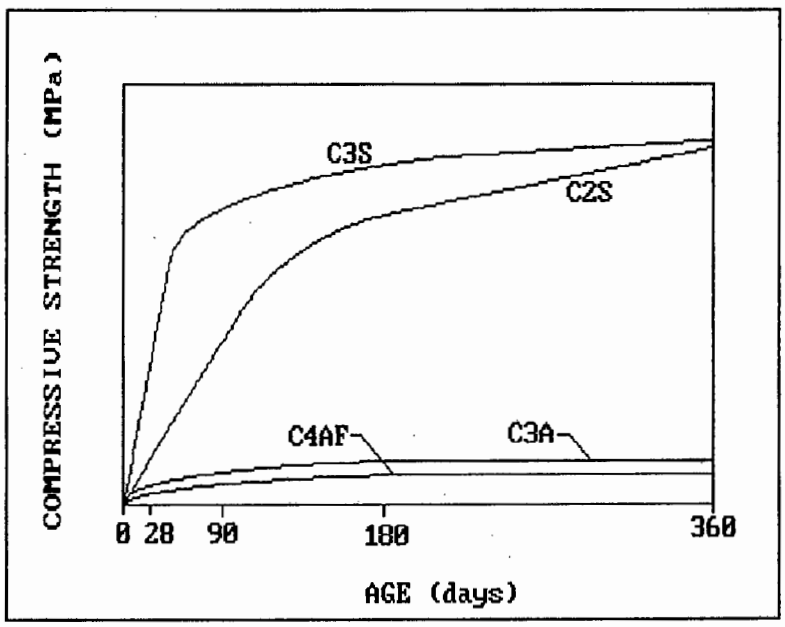

Figure 9 : Rates of strength development of neat pastes of pure compounds (reference 5.1).

Considering the above influences the chemical composition has on the strength of cement, there is a definite relationship between the degree of hydration and the rate of strength development. Thus, the chemical composition has the potential to cause a variation in the compressive strength of the hardened cement paste if the percentage of each compound varies from batch to batch.

5.2 CHEMICAL COMPOSITION : MAJOR COMPOUNDS

Portland cement is a complex non-homogeneous mixture containing four principal phases. The chemical composition of the cement is known but does not conform to a strict combination because the major compounds or phases can be contaminated with impurities or take up a slightly different form.

The clinker consisting of the four principal phases is essentially four crystalline compounds of calcium, two with silica, one with alumina and one with alumina and ferric oxide.

The combined content of the four compounds is approximately 90% of the cement weight, made up as follows :

TABLE 9 : AMOUNT OF EACH MAJOR COMPOUND IN CEMENT

MAJOR COMPOUND	PERCENTAGE (WEIGHT)
C_3S	35-55
C_2S	20-40
C_3A	5-12
C_4AF	5-10

The four major compounds each influence the properties of the cement differently. Most importantly, the quantities of each can cause variations in strength, the rate of evolution of heat of hydration and the resistance of cement to sulphate attack. The effect of each major compound needs to be dealt with in greater detail :

5.2.1 TRICALCIUM SILICATE (C_3S)

Tricalcium silicate (C_3S) is the primary cementing compound in Portland cement and is chiefly responsible for its early strength development (ie. the first four weeks)[5.2, 5.4, 5.7, 5.8].

C_3S is unstable at temperatures below 1250°C. It breaks down to C_2S below 1250°C but below 700°C C_3S exists indefinitely. Thus, during the clinker cooling stage, after leaving the burning zone, the clinker is cooled at such a rate to retain as much C_3S as possible.

The degradation of C_3S to C_2S is due to slow cooling. The slow cooling causes a reaction between the melt and the C_3S resulting in C_2S and C_3A. Thus the rate of cooling in the cooler is such to prevent the degeneration of the C_3S to C_2S.

C_3S usually exists in the monoclinic form in Portland cement and is generally referred to as "Alite".

Alite is the impure form of C_3S. It contains small amounts of other oxides in solid solution. Alite thus contains small percentages of Al_2O_3, Fe_2O_3, Na_2O and K_2O. These impurities affect the strength of C_3S. These impurities have been monitored throughout the research period via the "Bogue method" in an attempt to ensure that they did not vary significantly. A thorough investigation of the influence of the impurities however was beyond the scope of this dissertation.

5.2.2 DICALCIUM SILICATE (C_2S)

Dicalcium silicate hydrates slower than tricalcium silicate and is mainly responsible for the strength gain in cement after 28 days[5.5, 5.6]. Belite is the impure form of C_2S and usually contains impurities such as aluminium, ferric and alkali oxides.

Above 650°C to 670°C C_2S exists in other forms but below this limit it remains in the βC_2S form. All references to C_2S in this thesis are to the βC_2S form unless otherwise stated. Of all the different forms of C_2S, only βC_2S exhibits cementitious properties.

There are four forms of C_2S, namely αC_2S, $\alpha' C_2S$, βC_2S and γC_2S. The γ-form is almost inert[5.9], the α-form gives very poor strength and the α'-form is non-hydraulic[5.3]. The hardened paste (βC_2S) gains strength steadily and slowly for weeks and months reaching a final strength usually of the same order as that of C_3S[5.5].

5.2.3 TRICALCIUM ALUMINATE (C_3A)

C_3A is not regarded as a hydraulic cement since a hydrated paste of C_3A dissolves in water. C_3A is reputed to affect the rate of hydration of C_3S and alternatively is said to gain low strengths for up to a day or two[5.5, 5.10, 5.11]. The contribution that C_3S makes to strength during these early stages is not greatly dependant on the C_3A content of the cement. Dependency increases with time, and maximum dependency occurs at about 28 days[5.12]. C_3A operates by accelerating hydration rather than by changing the cementitious properties of the hydration products. This is still a controversial topic as certain authors believe that C_3A contributes to the strength during the first few days while others believe it contributes little or nothing to strength and is undesirable in cement.

In its pure form C_3A reacts with water almost instantaneously producing a "flash set", accompanied by high heat of hydration. Gypsum (Calcium Sulphate di-Hydrate : $CaSO_4.2H_2O$) is added to prevent the flash set.

Tricalcium aluminate also acts as a flux in the kiln thereby reducing the burning temperature of the clinker. It is essential (along with C_4AF) to facilitate the melt fusing of CaO and SiO_2. However, hydrated tricalcium aluminate is unstable in water and is sensitive to sulphate attack. Therefore the presence of tricalcium aluminate in cement is therefore undesirable[5.6].

5.2.4 TETRACALCIUM ALUMINOFERRITE (C_4AF)

It is unclear whether C_4AF contributes to the strength of hydrated Portland cement. According to Mironov and Malinina[(ref 5.10) pg8 fig 1.6], C_4AF reaches the strength of C_3S at a similar rate.

The graphical facts illustrated in Figure 10 are contradicted by Bogue and Lerch (Figure 9) who show C_4AF to exhibit almost no strength qualities. The literature is vague concerning C_4AF although the majority of the more recent publications tend to favour C_4AF as having no strength related properties. According to Fulton[5.5], Tetracalcium Aluminoferrite hydrates rapidly, and develops very little strength. Alexander[5.12] is of the opinion that there is only a weak association between C_4AF and strength.

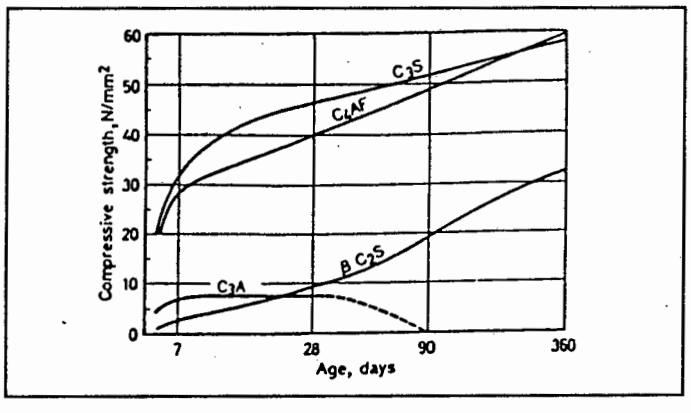

Figure 10 : Rates of strength gain of neat pastes of pure compounds : according to Mironov and Malinina (ref. 5.10).

The C_4AF phase in Portland cement clinker is also known as brown-millerite[5.3].

5.2.5 MAJOR COMPOUNDS OF RELEVANCE

The effect that each compound has on strength has been determined to a degree where it is accepted that both tricalcium silicate and dicalcium silicate have the major effect on strength. However, all the available literature has conflicting points of view with respect to the effect tetracalcium aluminoferrite and tricalcium aluminate have on strength. Therefore, it was necessary to analyse all four of the major compounds.

5.3 CHEMICAL COMPOSITION : MINOR COMPOUNDS

5.3.1 MAGNESIA (MgO)

Magnesium oxide (magnesia) is formed when $MgCO_3$ is dissociated on burning. The raw materials used for cement manufacture usually contain a certain amount of dolomite ($MgCO_3.CaCO_3$). Up to 5% of the magnesia can be dissolved in the clinker liquid and the remainder of the uncombined magnesia would be present as free magnesia, burnt magnesia or periclase in the finished product.

The hydration of the periclase causes an increase in the volume of the hardened concrete and may cause "unsoundness". Gonnerman, Lerch and Whiteside[5.13] found that the primary cause of unsoundness of Portland cement was the free CaO and crystalline MgO contents of the mix. Unsoundness can be defined as undue volume changes, warping or cracking of cement paste[5.5]. The degree of unsoundness depends on the crystal size. The smaller crystals tend to hydrate more rapidly without setting up internal pressures. Slow cooling allows crystal growth.

$MgCO_3$ is a minor constituent of most raw materials, but if it is present in excessive quantities, exposure of the resulting concrete to moist conditions may, over a period of years, result in expansion of the cement paste and deterioration of the structure[5.5].

5.3.2 FREE LIME (CaO)

Free lime is found in cement when the raw materials used have more lime than can combine with the acidic oxides SiO_2, Al_2O_3, Fe_2O_3. The CaO present in the cement is formed when $CaCO_3$ dissociates as the raw materials are burned, it is often referred to as "dead burnt lime" because "CaO" can also be part of a more complex compound (ie. not free lime). The excess lime formed during burning is intercrystallised with other minerals and not readily accessible to water. Therefore, when concrete is mixed with cement which has free lime, the free lime will usually only hydrate after the cement has set. Hydrated lime has a greater volume than the free CaO. Thus, when the lime eventually hydrates, it causes an expansion of the set cement, ultimately resulting in the cracking and deterioration of the cement/concrete.

5.3.3 ALKALI OXIDES (K_2O, Na_2O)

The alkali oxides K_2O and Na_2O first combine with sulphur trioxide (SO_3) in the melt resulting in

a solid solution of sodium-potassium sulphate ($3K_2SO_4.Na_2SO_4$). The remaining alkali oxides not used in this reaction then combine with dicalcium silicate (C_2S) and tricalcium aluminate (C_3A).

When alkali-reactive aggregates are used in concrete production they react with the alkali oxides forming an alkali-silica gel which has expansive tendencies. The alkali-aggregate reaction causes cracking and deterioration.

5.3.4 PHOSPHORUS PENTOXIDE (P_2O_5)

Phosphorus pentoxide (P_2O_5) reduces the rate of hydration of Portland cement (in the initial stages) as it is responsible for breaking C_3S down to C_2S. Generally, the P_2O_5 content does not exceed 0.2% although sound cements with a 2.0% to 2.5% P_2O_5 content can be produced.

5.3.5 GYPSUM ($CaSO_4.2H_2O$)

The reaction of tricalcium aluminate (C_3A) with water is violent and leads to the immediate stiffening of the paste more commonly known as a "flash set". The setting time or flash set is controlled by the sulphate content which is added in the form of gypsum.

On the addition of water the gypsum is dissolved forming a calcium sulphate solution and the C_3A begins its rapid reaction with water to form a calcium-aluminate hydrate. The calcium sulphate reacts with the calcium-aluminate hydrate forming ettringite ($C_3A.3CaSO_4.32H_2O$).

Ettringite is insoluble in water and is deposited on the C_3A crystals forming a barrier around the crystal. Water works its way through the barrier resulting in further hydration of the C_3A which is once again sealed off by the calcium sulpho aluminate. This mechanism slows the rate of hydration and can be controlled by the amount of gypsum added. If too little gypsum is added, the cement will tend to set quickly.

An excess of gypsum leads to expansion causing unsoundness. This occurs if gypsum is present in excess of the amount that can react with C_3A during hydration and will cause unsoundness in the form of slow expansion[5.6].

The effect that gypsum has on strength has been researched extensively and the conclusion drawn by Alexander[5.12] was that there was no consistent evidence that the sensitivity of the chemical

compounds varied with the gypsum content. This is a controversial issue as much research contradicts Alexander's[5.12] conclusion.

5.3.6 MINOR COMPOUNDS OF RELEVANCE

It may be necessary to monitor all the minor compounds as they all have some effect on strength.

5.4 CONCLUSIONS

From the investigation and literature review conducted into the chemical composition of ordinary Portland cement, the following can be concluded :

1. The conditions that clinker is subjected to during both the burning and cooling stages of manufacture can cause the chemical composition to vary.

2. The two major compounds, tricalcium silicate (C_3S) and dicalcium silicate (C_2S) have a direct influence on the strength of cement.

3. Tricalcium silicate (C_3S) will have a greater influence on the 28 day strength of hardened cement paste (hcp) than dicalcium silicate (C_2S), although the contribution to strength of each compound should be equivalent at later stages.

4. Only the βC_2S form of C_2S exhibits cementitious properties.

5. Tricalcium aluminate (C_3A) influences the rate of hydration of tricalcium silicate (C_3S) and may also contribute directly to strength for up to three days. This is a controversial issue and the literature reviewed contained many conflicting opinions.

   C_3A is not regarded as a hydraulic material because its hydrated form is dissolvable in water.

6. Tetracalcium aluminoferrite (C_4AF) has no strength related properties but this has not been clearly established in the literature reviewed. The effect that C_4AF has on strength should be investigated further.

7. The minor compounds in cement influence the strength of hcp and need to be monitored to ensure they do not vary significantly.

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CHAPTER 6

CHEMICAL ANALYSIS

6.1 INTRODUCTION

Cement is a mixture of fine-grained minerals. The separation of these minerals, by chemical or mechanical means, is rather difficult, if not impossible. Consequently, the determination of the chemical composition of these minerals and their content in the cement clinker have presented some difficulty.

The elements are normally analysed by X-Ray fluorescence but compounds can also be determined by X-Ray diffraction. There are other direct methods such as optical microscopy but this method is subject to considerable error due to the difficulty in locating the limits of each grain, while the sample and area viewed is not always representative of the batch.

The standard analysis of cement in South Africa is performed by X-ray fluorescence which determines the elements in the cement quantitatively. This is followed by the Bogue analysis which combines these elements into compounds. This method has many shortcomings and although it was investigated initially in this research, the X-ray diffraction method was chosen in preference, as it is a direct quantitative analysis of the compounds in the cement.

Both the X-ray diffraction and the X-ray fluorescence methods and their associated problems are described below.

6.2 X-RAY DIFFRACTION

Since 1958 there have been several attempts to use X-ray diffraction analysis for determining the compound composition of cement[6.1]. X-ray diffraction can be used in three principal ways :

a. analytically - for the identification of unknown compounds.

b. quantitatively - for the estimation of the phases present in a mixture.

c. structurally - to determine information about the constitutions of individual compounds.

The accuracy of this method is open to serious question[6.2]. However, the alternative and accepted method of predicting the compound composition, the Bogue method, is also subject to serious error[6.2] and it is usually considered that the X-ray diffraction method is, in principle, the better analytical method[6.3].

The quantitative estimation of the compound phases, using X-ray diffraction, is based on the premise that the integrated intensity of a reflection is directly proportional to the amount of the substance producing it[6.4, 6.5].

X-ray diffraction was chosen as the instrument for investigating the amount of each compound in Portland Cement for the following reasons :

1. X-ray fluorescence (XRF) is an indirect method for analysing the compounds in cement. The results of an XRF test only indicate a potential chemical composition because of the assumptions used during further Bogue analysis.

   When discussing the analysis of cement by X-ray fluorescence, Fulton[6.6] states that "The mineral composition of any particular clinker cannot be established with any high degree of accuracy".

2. X-ray diffraction (XRD), on the other hand is a direct method of analysis and can be used to indicate the chemical compound composition, by the integration of intensity peak areas.

3. As recently summarised by Taylor[ref.6.4 p119], the four major clinker phases may be satisfactorily determined by XRD. The absolute accuracy is about 2% to 5% for alite and belite and between 1% and 2% for the aluminate and ferrite phases.

4. Although many difficulties are encountered in the compound composition or phase identification and analysis of cement by XRD, the method is shown to be accurate (Struble[6.7]).

X-ray diffractometry is mainly used for the identification of compounds by their diffraction patterns. A diffractometer utilizes a monochromatic beam of radiation to yield information about the interplanar spacing of the crystal lattice and the reflected intensities of X-rays received from a single crystal or crystalline powder[6.8]. The X-ray region is considered to be that part of the electromagnetic spectrum lying between 0.1 -100Å (Å = 10^{-9}mm)[6.9].

X-ray diffractometry deals with crystalline materials. A crystalline substance has a definite characteristic

form which is retained regardless of the physical size of the crystal[6.10].

The Bragg law is used to determine the interplanar spacing of a compound or element, or to determine the angle at which a diffracted x-ray would be visible if it were diffracted off that crystal.

The Bragg Law takes no account of the refraction of X-rays but since this effect is very small (the index of refraction is of the order of 0.99999) it has been ignored[6.8].

Referring to figure 13 (Condition for diffraction of X-rays), for the X-Rays to be non-destructive the length CD must equal a whole wavelength(s).

ie.	$CD = 2\varkappa$	and	$\varkappa = d.SIN\ \theta$
for	CD = 1 wavelength	$\therefore$	$2\varkappa = 2d.SIN\ \theta$
for	$CD = \lambda$	$\therefore$	$\lambda = 2d.SIN\ \theta$

Thus, the Bragg Law can be formulated as :

$$n\lambda = 2d.Sin\ \theta$$

Where the path length difference between CBD is equal to a whole wave length the constant 'n' takes on a value of 1.

The reflected rays are only 'visible' outside the lattice if, after reflection against the individual planes they are out of step by a whole wavelength or a number of whole wavelengths. When this is so the reflected rays re-enforce one another. If the wavelengths are out of step by any portion of a wavelength then the reflected rays tend to cancel one another out. This phenomena is known as "interference" and was formulated by Sir William Bragg.

An electron which is situated in an alternating electromagnetic field will oscillate with the same frequency as the electromagnetic field. Since an X-ray beam can be considered to be an electromagnetic wave travelling through space, it too will cause all electrons in its path to oscillate[6.7]. The electron waves combined give the resultant wave of the X-ray.

The optical configuration of the X-ray diffraction can be seen in Figure 11.

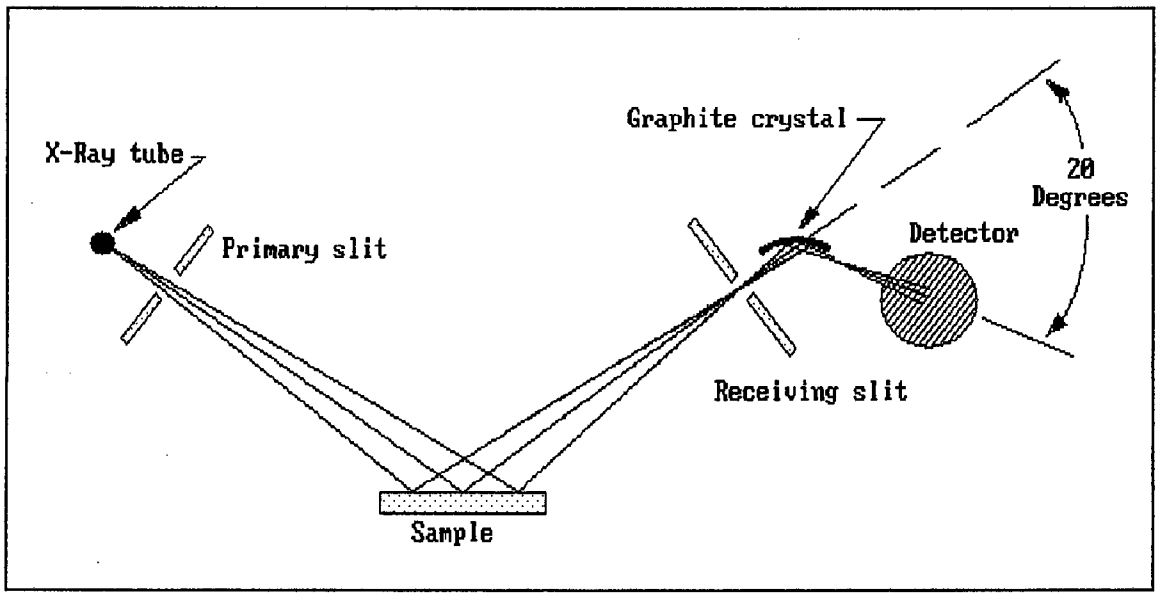


Figure 11 : Optical configuration of an X-ray diffractometer

In order for diffraction to occur a beam of monochromatic X-rays must fall onto a crystal lattice which is a regular arrangement of atoms. The diffracted beams or emitted waves must be in phase with each other in the direction of observation.

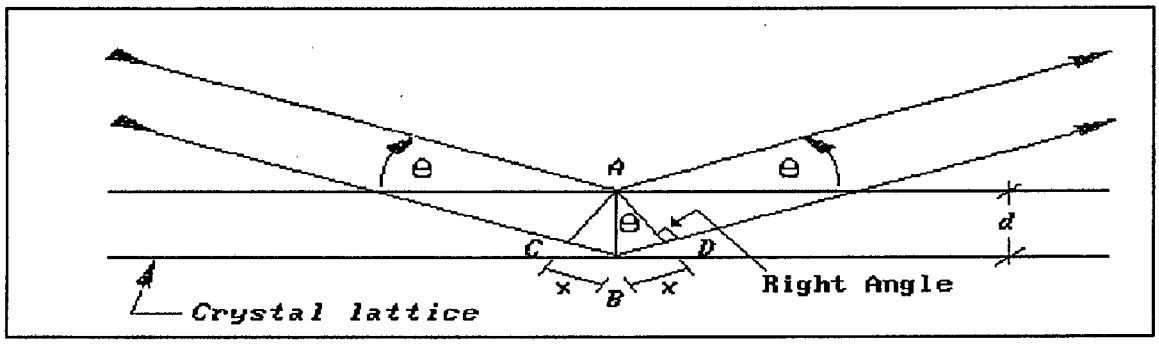


Figure 12 : Condition for diffraction of X-Rays

This condition is illustrated in Figure 12 and is easiest to visualise if the crystal lattice is seen as a set of parallel planes separated by distance "d". This distance represents the interplanar spacing of the crystal lattice.

Two parallel rays strike a set of crystal planes at an angle θ and are scattered. When the difference ($2x$) between the path lengths of the two rays is equal to a full wavelength, reinforcement occurs and the rays are non-destructive.

6.2.1 EQUIPMENT

The equipment required for X-ray diffractometry consists of three basic parts :

(a) A source of radiation, consisting of an X-ray tube (Cu tube) and high voltage generator.

(b) The diffractometer

(c) Detector and counting equipment

The function of the generator and the X-ray tube is to provide a stable source of radiation. The radiation is reflected off the sample in the diffractometer (Appendix 3 shows a typical diffractometer) and the detector's function is to convert the individual photons into voltage pulses. The voltage pulses are then counted by the counting equipment giving various forms of visual indication of X-ray intensity.

The intensity measurements were carried out on a Phillips X-ray Powder diffractometer. The radiation used was Cu-K-alpha obtained from a tube operating at 40kV and 30mA. A goniometer with a step scanning device was used and the samples have thus been tested on a step basis. The optical system used consists of a 1° divergent and receiving slit.

All diffraction patterns were recorded on a computer and transferred to a spreadsheet package and analysed.

6.2.2 BASIC ASPECTS OF THE FOUR MAJOR PHASES OF PORTLAND CEMENT BY X-RAY DIFFRACTION

Portland cement represents a multi-component system of more than four phases, causing numerous difficulties in quantitative analysis when using X-ray diffraction methods. These "difficulties" or problems were overcome and are discussed at a later stage. In general the coincidences and superposition of the compounds are shown by the X-ray diffraction pattern of a typical Portland cement, scanned over the angular region from 55.0 to 25.0 2θ, as shown in Figure 13.

The principal reflections of the two calcium silicates, which usually constitute approximately 70 percent of the cement clinker, coincide or overlap considerably. There are only a few minor reflections of the β-C_2S(A) and C_3S(B) phases which are not influenced by mutual interference, as can be seen in Figure 13.

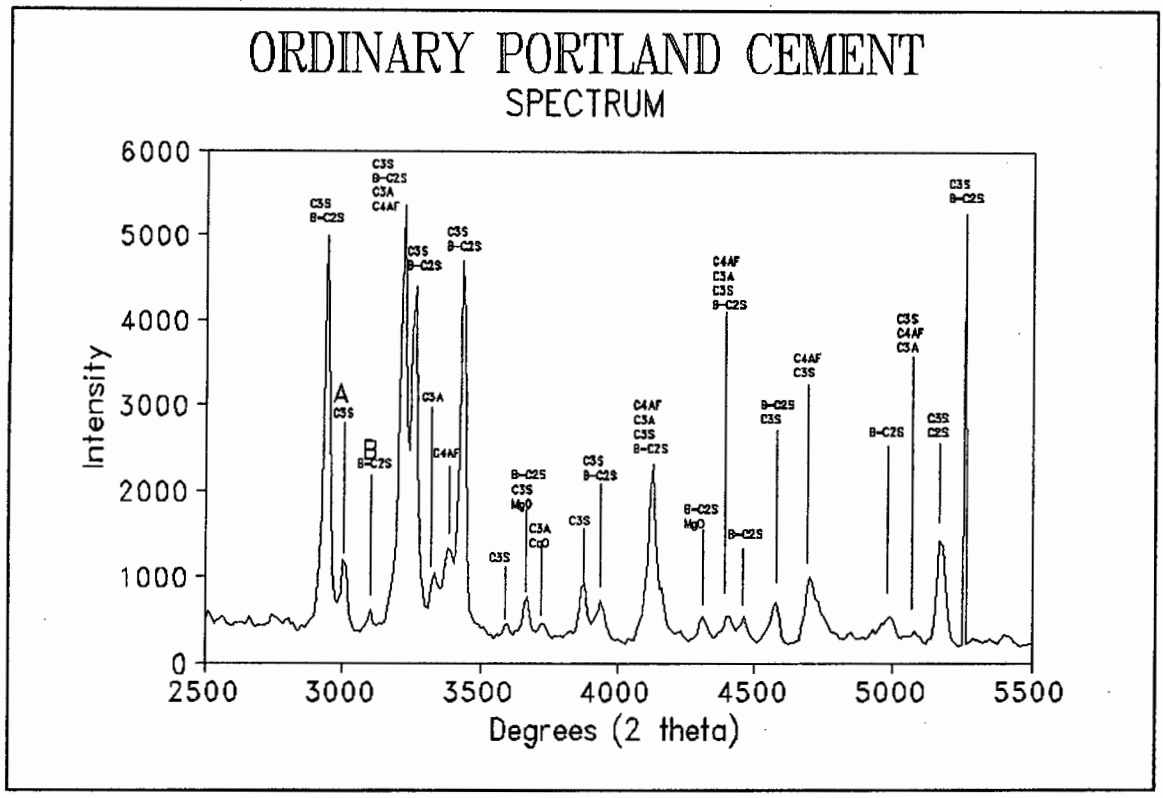


Figure 13 : X-ray powder diffraction pattern of typical Portland cement. The peak specifics were obtained from Pretoria Portland Cement (PPC).

The peak due to β-C_2S at 2.873Å (31.1°2θ) is free from interference but is weak. By adjusting the diffractometer for high resolution and working with a scanning speed of 0.3°2θ per minute, this diffraction line can be used for analysis, provided its concentration in the cement is sufficient. In addition, Figure 13 indicates that for the determination of the C_3S phase, a suitable line at 2.964Å (30.1°2θ) exists.

The C_3A and C_4AF phases are fairly well registered in the pattern of Figure 13. The reflection represented by the diffraction line at 2.691Å (33.2° 2θ) was therefore used directly for the determination of the concentration of the C_3A phase. Similarly, for the determination of the concentration of Tetracalcium aluminoferrite, the reflection conforming to the diffraction line at 2.634Å (34.0°2θ) had to be used. These phases cannot be recognised if the clinker contains a very low percentage of either of these compounds. In the cements analysed from De Hoek (PPC) the C_3A content is approximately only 2% whereas Ordinary Portland Cement usually contains between 5% and 12%. Thus, in Figure 13, the peak at 2.691Å (33.2°2θ) representing C_3A is not very visible.

In the angular region (in Figure 13) from 35.0 to 28.0°2θ (identified in Figure 14) the relevant diffraction lines of the four clinker phases are encountered. Figure 14 represents an enlarged section of Figure 13 showing the peaks more clearly.

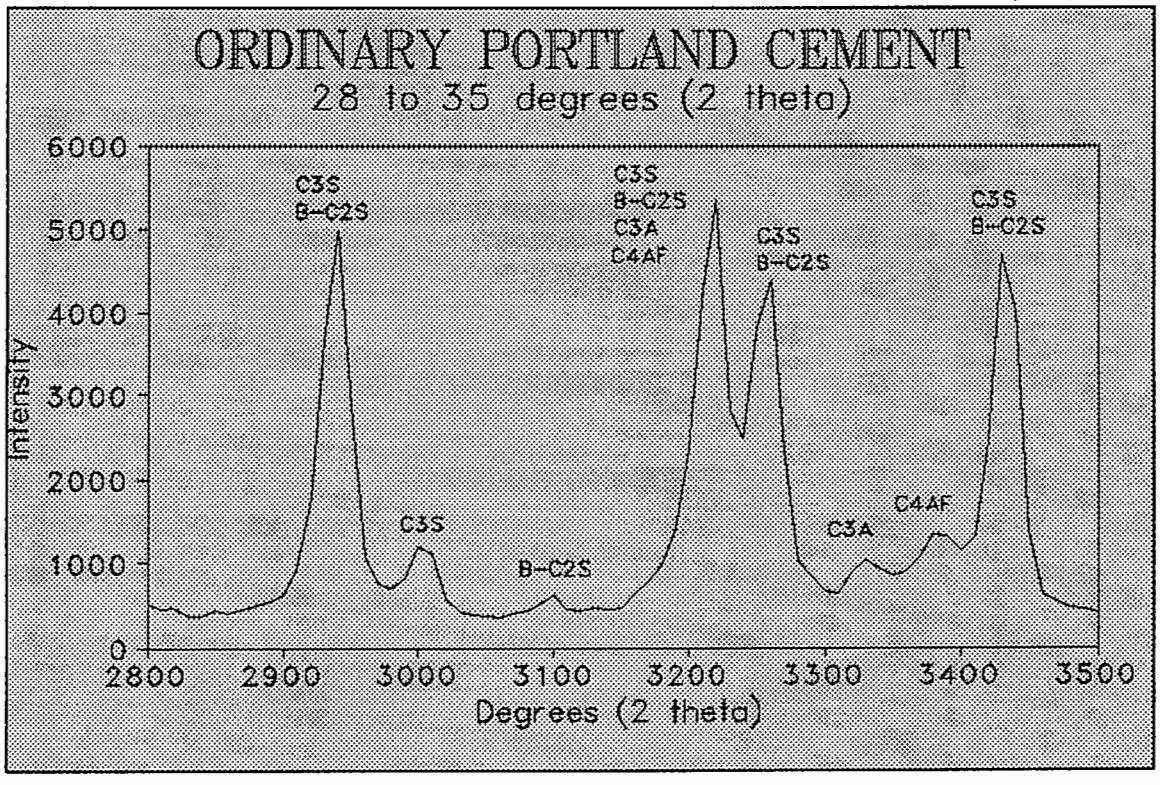


Figure 14 : X-ray powder diffraction pattern between the 2θ angles 28° and 35°

The d-values 3.025Å, 2.772Å, 2.739Å and 2.602Å are due to the reflections from the two main calcium silicates. The compounds C_3A, C_4AF and CaO all contributed to the interplanar spacing at 2.772Å.

The diffraction angles and corresponding interplanar spacings used for analysing the cement in this dissertation are given in Table 10.

TABLE 10 : IDENTIFICATION OF PHASES

Phase	X-ray diffraction angle 2θ	Interplanar spacing Å
C_3S	30.1	2.964
C_2S	31.1	2.873
C_3A	33.2	2.691
C_4AF	34.0	2.634

Graphs of the individual compounds are attached in appendix 7.

The interplanar spacings or "d" spacings for standard pure compounds are known and the diffraction angles can be calculated from the "d" spacings using the Bragg equation referred to earlier. Since the gypsum form in the cement was unknown, the peak identification was done in the above manner for three common gypsum types in an attempt to discover which type of gypsum was present in the cement. A more complete table of the interplanar spacings and relevant angles is attached in Appendix 4. The calculation was performed for the following three types :

1. Calcium sulphate di-hydrate ($CaSO_4.2H_2O$)

2. Calcium sulphate hydrate ($2CaSO_4.H_2O$)

3. Calcium sulphate ($CaSO_4$)

The diffraction angles and corresponding interplanar spacings in Table 11 were calculated using the Bragg law.

TABLE 11 : DIFFRACTION ANGLES AND INTERPLANAR SPACINGS

1			2			3		
d (Å)	%	BRAGG ANGLE	d (Å)	%	BRAGG ANGLE	d (Å)	%	BRAGG ANGLE
7.56	100	11.71	3.87	6	22.98	6.01	95	14.74
4.27	50	20.80	3.49	100	25.52	3.46	45	25.75
3.79	20	23.47	2.85	35	31.4	3.00	100	29.78
3.06	55	29.19	2.33	20	38.68	2.80	50	31.94
2.87	25	31.20	2.21	20	40.87	2.71	4	33.03
2.77	28	32.33	2.18	8	36.33	2.70	2	33.13
2.53	1	35.48	2.09	10	43.38	2.14	10	42.33
2.50	6	36.00	1.87	16	48.72	2.13	6	45.84
2.08	10	43.51	1.75	12	52.31	1.84	12	49.48
2.07	8	43.66	1.65	14	55.78	1.73	4	52.76
1.89	16	47.93	1.52	4	60.73	1.70	8	54.17
1.88	10	48.44	1.52	2	61.17	1.67	8	55.16
1.80	4	50.84	1.40	4	66.93	1.50	2	61.81

* **Note** : "%" represents the degree of intensity with respect to the largest peak of that kind in the spectrum

6.2.4 EXPERIMENTAL DETAILS

6.2.4.1 Preparation of the Sample

The sample was loaded into an aluminium diffraction slide (sample holder). The diffraction slide is closed on the base and sides and loaded from above. The sample holder is illustrated in figure 15.

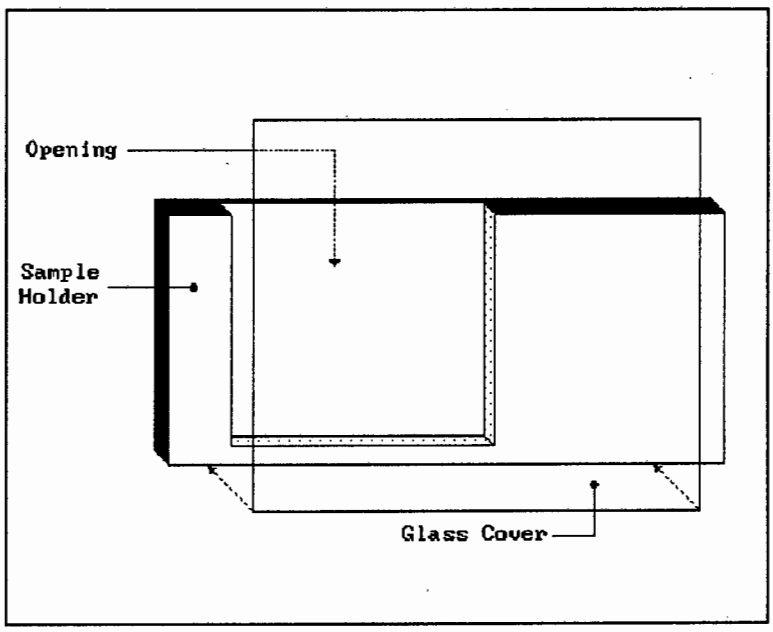


Figure 15 : Aluminium sample holder

The sample was then poured into the diffraction slide and carefully smoothed off using a glass plate. The possibility that the smoothing effect could cause preferential alignment of the crystals was considered and different methods were used in an attempt to prevent this from occurring. The sample was then loaded into the Phillips X-ray powder diffractometer, the divergent and convergent slits were chosen and the machine was sealed against radiation leakage.

Powders for investigation by X-ray diffraction must meet certain requirements in order to yield satisfactory and reproducible intensities. These requirements are dealt with below.

6.2.4.2 Preferential Alignment

Preferential alignment can cause variations in intensities. There are two theories on preferential alignment. Firstly, that the cement may already be partially hydrated because of moisture in the air and would thus prefer a particular orientation, especially when being smoothed off by glass. Secondly, that the crystals are imbedded in a matrix formed during clinkering and are thus randomly

aligned and any smoothing effect cannot cause preferential alignment. Preferential alignment can be identified by variations in peak heights when testing repeat samples.

Techniques were developed in an attempt to prevent preferential alignment, should it occur. The aluminum holder with its one side removed (Figure 15) had a glass plate clamped to the open side. The holder was then placed standing up and the cement sample was dropped into the opening while the holder was being tapped to compact the sample. The cavity was filled to capacity, the powder was compacted by tapping the container, and the excess scraped off. The glass plate was then carefully removed taking care not to slide it and cause orientation. The results of repetitive testing did not show any significant change in intensity when compared together indicating that the precision was good. Preferential orientation can be identified by variations in peak heights and peak ares's on repetitive testing of the same cement sample.

A second technique was also attempted. Glue was placed in the base of the holder and the cement sample was sprinkled over the glue in order to have a random alignment of the crystals. The results of this method were too varied and it was decided to use the standard method. The variation in the glue method may have been due to the penetration of the X-rays into the glue or because the thickness (height above the sample holder) of the sample varied.

According to Butcher[6.9] well controlled sample preparation of clinkers does not appear to introduce major orientation problems. If orientation occurs it is set in the matrix during cooling.

6.2.4.3 Sample Height

Peak shifts are caused by several factors, one of which is sample height, as diagrammatically shown in Figure 16.

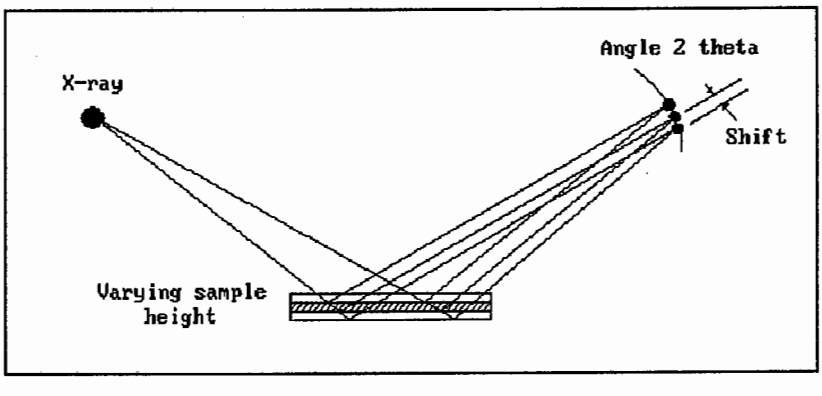


Figure 16 : Peak shift due to sample thickness

The shift of the peak position can cause difficulties in the identification of a substance in the sample. This was overcome by ensuring that the sample height was level with the top of the sample holder.

6.2.4.4 The effect of particle and crystal size

The effect which crystal and particle size have on intensity should be minimised. The grain size of the cement sample must be small enough for the absorption of the X-rays to be negligible. However, it must be large enough to be representative of the powder as a whole. An ideal specimen has a particle size of between 1 and 50 microns.

The crystal size is also of relevance because it effects the width of the diffraction peak. Where the crystals are very small (< 1 micron) the diffraction lines broaden by an amount dependant upon the mean crystal dimension, conversely, the peak base for larger crystal sizes diminishes as the crystal size increases. The crystal dimensions are affected by the cooling conditions which the clinker has been exposed to.

6.2.4.5 Sample Holders

Sample holders were available in either aluminum or perspex. Each sample holder, when analysed by X-ray diffraction gives a series of peaks representative of its own material. The series of peaks from the sample holders should not affect the final result of a test on a cement sample unless the X-rays are able to penetrate through the sample and reflect off the holder. It did not appear that this occurred as the peaks from the sample holder in Figure 17 were not evident in the X-ray diffraction results of the cement samples in Figures 14 and 13. An aluminum sample holder was used during this research as it had no peaks in the vicinity of the angles 2θ which were used for cement compound identification. The peaks from each holder are shown in figures 17 and 18.

6.2.5 CALIBRATION OF THE X-RAY DIFFRACTOMETER

In order to analyse the area under a peak and to determine the absolute quantity of a particular compound in a sample expressed as a percentage of the total chemical composition, it is necessary to compare the sample peak to that peak of a pure sample or a mix of pure compounds. It is necessary to test a pure sample of the relevant compound for comparative purposes. Unfortunately the scope of this research did not involve manufacturing

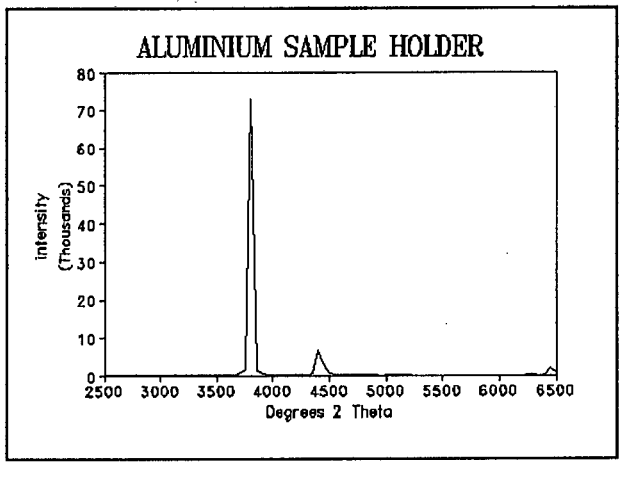


Figure 17 : Spectrum of an aluminum sample holder

synthetic samples of each compound (eg. tricalcium silicate). Synthetic samples are not manufactured or readily available in South Africa but can be obtained from institutions in Europe. In order to contain costs, this was not pursued. Instead, the compounds were represented as an intensity which either increases or decreases depending on the quantity of the compound present in a sample.

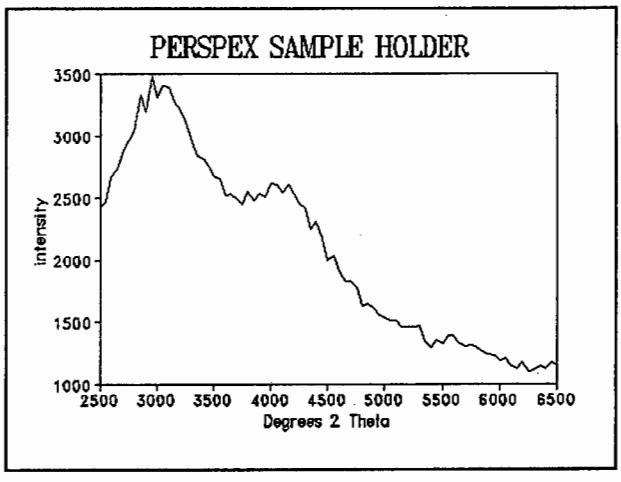


Figure 18 : Spectrum of a perspex sample holder

It was also necessary to check for instrument errors and consistency such as the alignment of the goniometer and the general efficiency of the X-ray diffractometer. This was done by using a silicon chip as a standard and checking the peak position and intensity of the output when the diffractometer was set up with specific constraints. The silicon standard was checked at both its prominent peaks (28.44°2θ and 56.10°2θ) where the intensity of the radiation from the Cu tube (40kV and 30mA) with a count time of 60 counts/min yielded intensities of 35 500 and 7 500 (diffracted X-rays received) respectively before background stripping occurred.

6.2.6 CALCULATION OF THE PHASE COMPOSITION

6.2.6.1 Peak Area Determination

The percentage of each phase (compound) can be calculated by determining the area under each respective peak once the background has been stripped. The area under the peak can then be compared to a standard from a cement of known phase composition or a synthetic sample consisting of 100% of that phase. The percentage of the phase present in the sample can then be determined.

The peak height is also representative of the percentage of the sample present, but this only applies if the shape of the peak area remains constant for all the samples tested. Should the peak broaden (ie. the side slope is decreased) then the peak height cannot be used as an accurate quantitative indicator.

Two methods were used to calculate the peak areas and the peak heights. The first used a polynomial to calculate the background and the second used a straight line (Figures 19 and 20

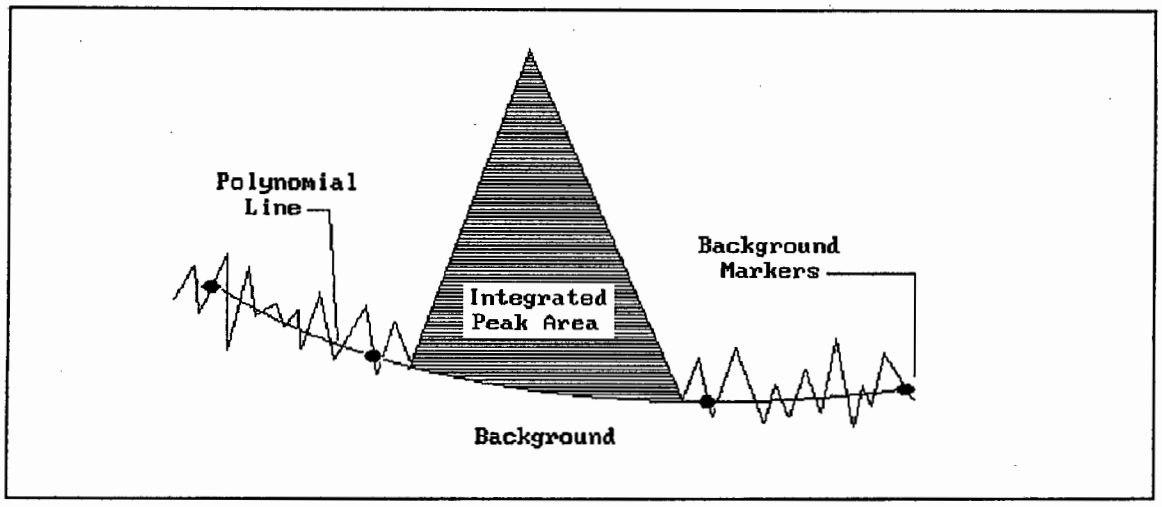


Figure 19 : 1st Method : Polynomial

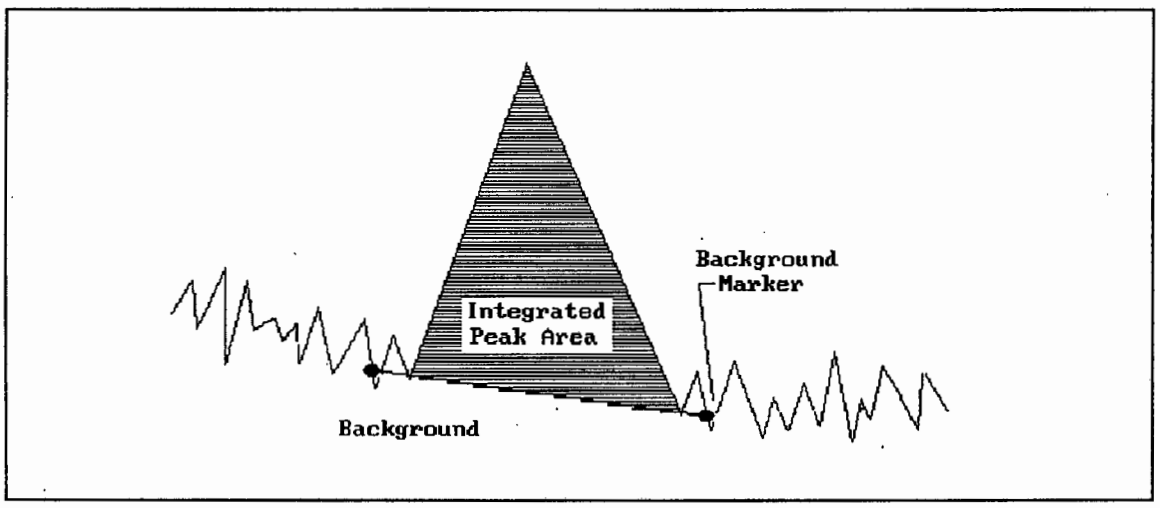


Figure 20 : 2nd Method : Straight line

respectively). The background represents the interference in the results within the diffractometer and background markers are used to define the background. The data was analysed separately using both methods in order that the accuracy of each method could be determined and a final method chosen.

The polynomial calculations showed a higher degree of variation than the straight line calculations when comparing the correlation coefficients of the areas of each method to the compressive strength of the samples. A significant error was apparent in both the polynomial and straight line calculation methods due to the position of the background markers (Figure 21 and 22). This effect appeared to be more pronounced in the polynomial method and causes a variation in the peak area as the base is the broadest section of the peak. The peak height is also affected significantly.

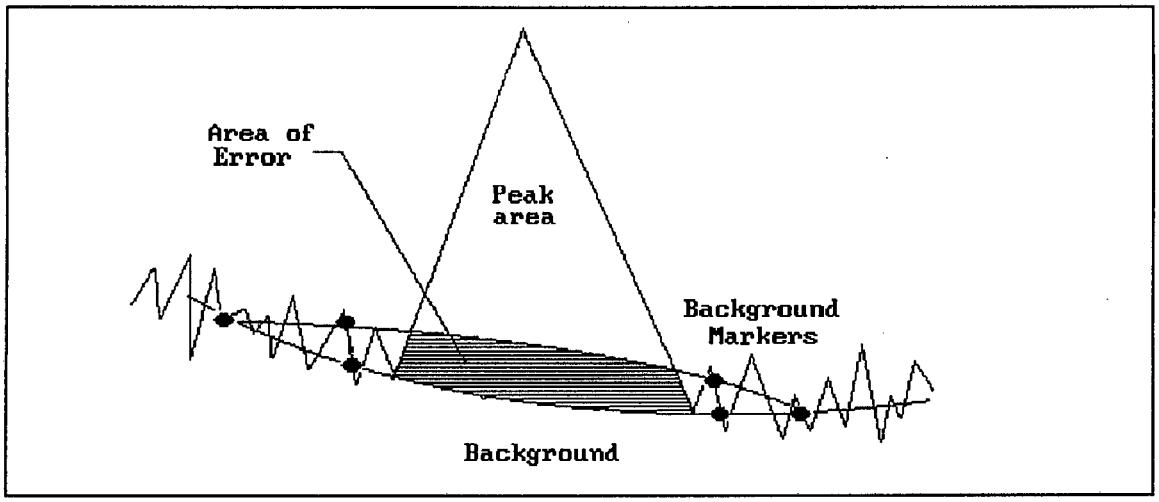


Figure 21 : Polynomial method background marker error

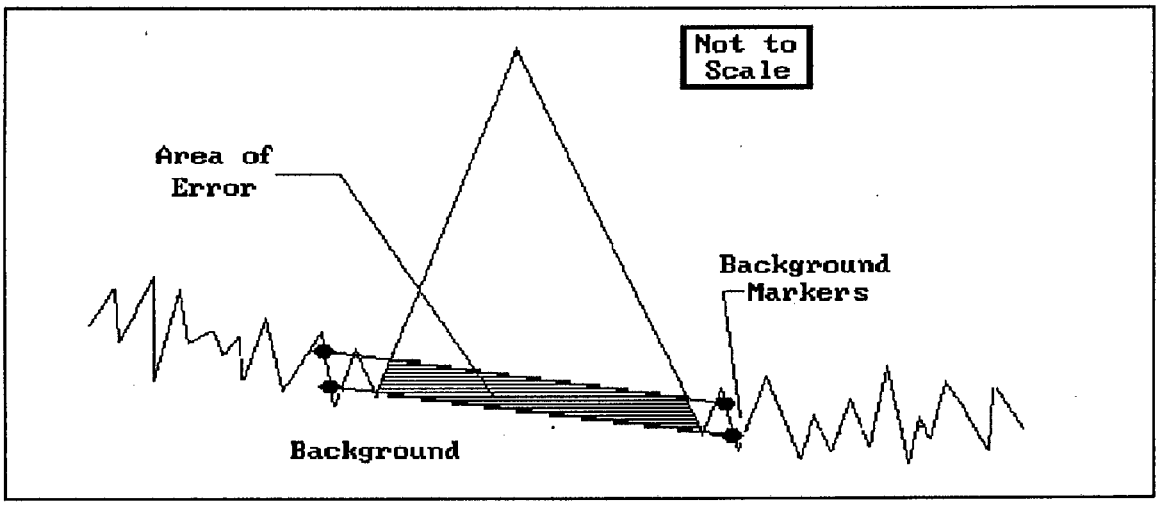


Figure 22 : Straight line method background marker error

The selected peaks were analysed using X-ray diffraction software developed at UCT (Author M.Kirby). This software <XPROC.EXE> provides background stripping, peak height and integrated peak area processing for the specified peaks.

The XRD data file was written using a 5 line header, as below, with the 6 line header containing information specifying the processing required.

Example

<FILE C_2S.XRD>

Data Line

Data Line

Data Line

Data Line

Data Line

601 20.0000 50.0000 0.0500 10.0000STEP202311 291

2000 103 10000

2005 125 10000

2010 137 10000

2015 152 10000

"

"

"

5000 100 10000

The file C_2S.XRD was the recorded data from the X-ray diffractometer and represented the position of the peaks.

The background associated with each peak was contained in the description file C_2S.XRS. The description file contained the following information:

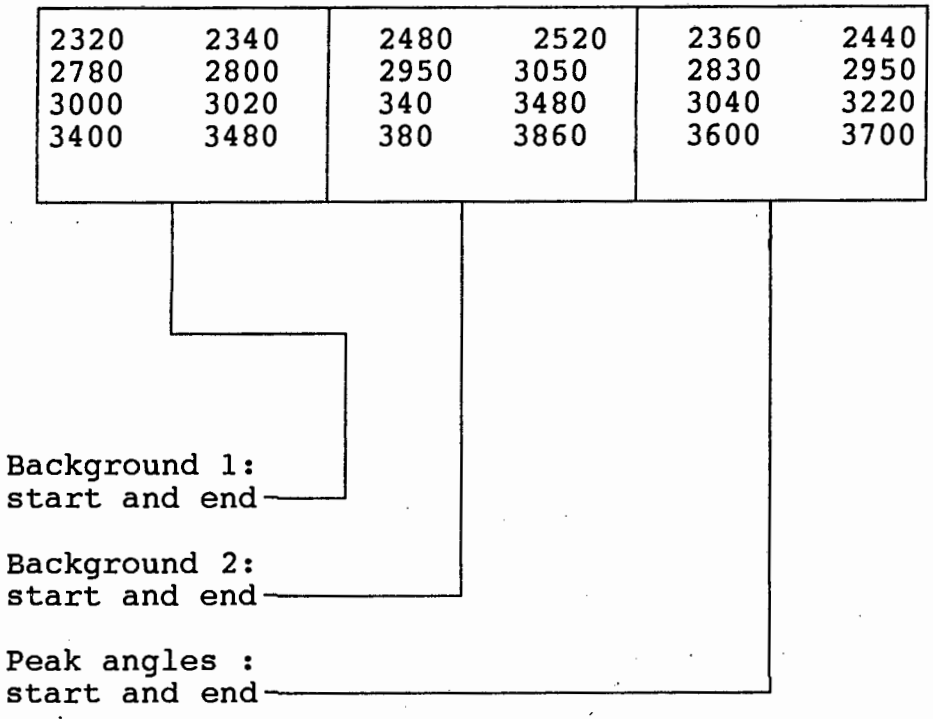
- The start and end 2-theta angles of the first region to be used as background.

- The start and end angles to be used as the second background region.

- The start and end of the region to be analysed as a peak.

The description file below (C_2S.XRS) specifies the four peaks to be analysed. The background for the first was measured from 23.20 to 23.46°2θ and from 24.8 to 25.2°2θ. The peak was measured between the angles 23.6 and 24.4°2θ.

FILE C_2S XRS >



Each peak was analysed as follows:

The total background under the peak was calculated by fitting a line through backgrounds 1 and 2 of the scan. The intensity of the background at any point under the peak was determined by interpolation.

The position of the maximum point was calculated and the value was obtained by substitution into the fitted curve. The background at the position of the peak was evaluated by summing the area under the curve with the background subtracted at each point.

The output of the program is a data file called $<C_2S.XRO>$, with the following format :

Processing file C_2S.XRO

#	THETA	D-SPACE	HEIGHT	AREA	HEIGHT	AREA
1	23.906	3.723	290.18	79.08	286.23	75.98
2	28.810	3.099	438.66	176.35	454.93	195.47
3	31.292	2.859	1814.09	713.60	1768.60	638.08
4	36.721	2.448	219.62	59.55	235.90	75.71

d-Space and
2-theta angle

polynomial line

Straight line

There are two values for each peak area and peak height, calculated using a straight line and a polynomial. The straight line is more useful where the noise inherent in the measurement may cause strange effects on the values calculated if a polynomial is used.

6.2.6.2 Peak Area and Height Consistency

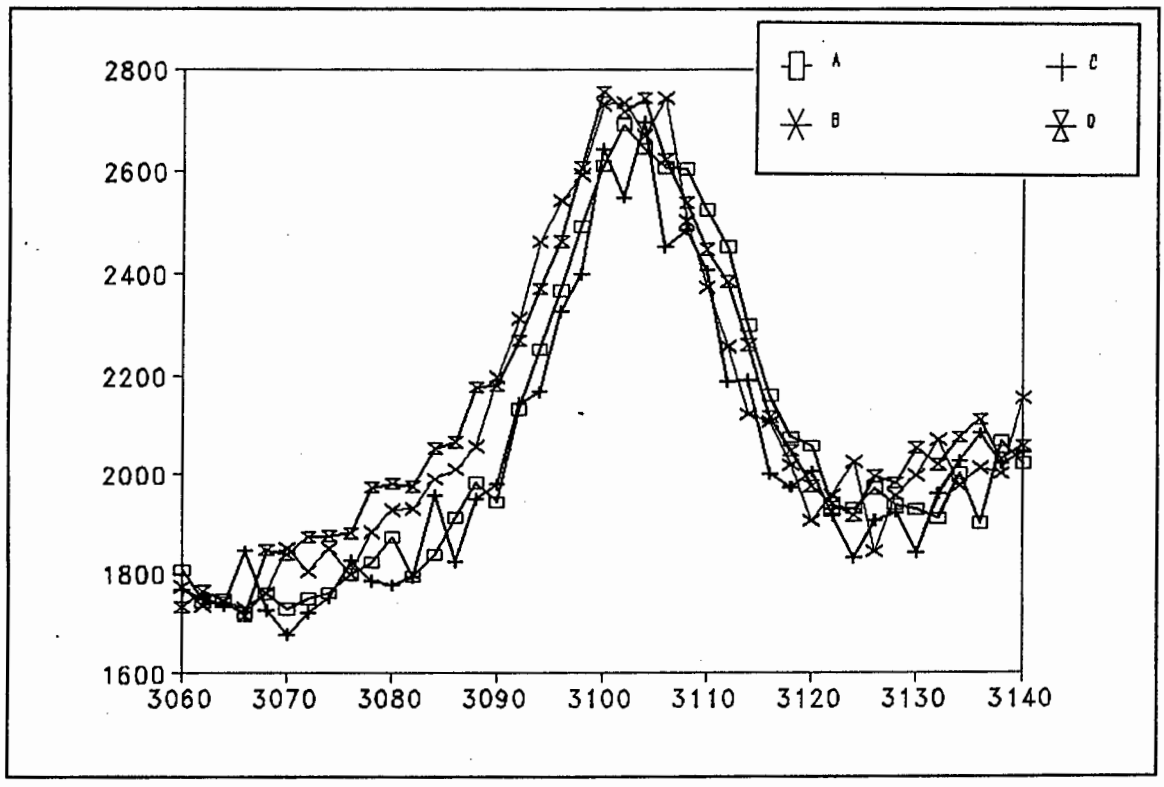


Figure 23 : The consistency of four separate XRD tests on the same sample

To check the consistency, firstly of the XRD analysis and secondly, of the peak area determination, four tests were run on exactly the same sample, each time remixing and re-testing the sample. The analysis of each sample was performed separately and the results were represented in two forms. Firstly, the four graphs were superimposed (represented graphically in figure 23) and secondly, the results of the peak area analysis were represented in a tabular manner (Table 12).

TABLE 12 : PEAK AREA AND HEIGHT TABLE

PEAK NO.	PEAK AREA	STANDARD DEVIATION	V%	PEAK HEIGHT	STANDARD DEVIATION	V%
A	19.41	0.814	3.883	85.85	2.894	3.183
B	24.64	1.145	5.287	96.88	3.474	3.823
C	22.23	0.331	1.528	94.18	1.915	2.108
D	19.92	0.634	2.927	86.54	2.496	2.747

By representing the dispersion of results on a percentage basis the results are compared by using a coefficient of variation. The coefficient of variation is a ratio of the standard deviation, ρ, to the mean, μ, and is defined as V.

$$V = (\rho/\mu) \times 100$$

The coefficient of variation (V) calculates a value that is independent of the units employed and is represented as a percentage.

The variations in peak area and peak height average 3.4% and 3.0% respectively. These variations are acceptable but can be minimised by preventing the preferential alignment of the crystals and by grinding the cements finer to prevent any large crystals dominating the surface area during X-ray diffraction.

As a further method to locate the mean of different samples, four repeat tests were run on each sample throughout the XRD work and the results were taken into account when comparing the XRD results to the compressive strength of the samples.

6.2.7 XRD PROBLEM AREAS

Although quantitative XRD gives a direct analysis of the phase composition of Ordinary Portland Cement and eliminates the problematic assumptions of XRF and other indirect methods of analysis, the method has certain problems which need attention :

1. There are no "standard" procedures for quantitative XRD analysis in South Africa. XRD procedures and methods for quantitative analysis do exist but they require sophisticated software packages which were not available for this research. As a result, the experimental procedures of most researchers differ considerably and it is up to the individual to decide how to measure peak intensities and what operating conditions to apply to the diffractometer. For example, the thickness of the sample and the density of the packed sample are variable.

2. The type of diffractometer and its operating conditions can cause variations between work performed at different institutions, as equipment cannot easily be calibrated to a single standard. The reason for this is that pure compounds are difficult to make, C_3S for example, cannot be made without C_3A or C_4AF. As a result, artificial methods are used and these differ from laboratory to laboratory. Also, the pure compounds degrade over time making universal calibration difficult.

3. Calibration of a particular diffractometer is also difficult as standard materials (of known chemical composition) are difficult to obtain and very expensive. Calibration against these standards of synthetic clinkers assumes the likeness of synthetic and industrial minerals which is difficult to verify as the industrial minerals in the clinkers are difficult to separate.

4. It is difficult to choose which peaks to analyse as many of them overlap with peaks from other compounds. There is no standard indicating which peaks to use. It depends on the individual operator.

5. Calibration of XRD results versus the potential compound composition is hampered due to the poor knowledge of the true chemical compositions of the phases at hand. The mere achievement of good correlation is no guarantee of the correctness of the calculated phase compositions. However, Struble[6.7] has indicated that the situation will be alleviated by a set of clinkers with known phase composition that is being developed by the National Institute of Standards and Technology (NIST).

6. The degree to which cement has hydrated can be affected by the storage conditions of the clinker. An example of this is a cement manufacturing plant in the Western Cape which stores its clinker in bunkers open to the elements. The rain saturates the clinker in the bunkers and the author estimates (very roughly) that between 5% and 10% hydration of the clinker could occur before the clinker is ground to cement. The degree of hydration will therefore be seasonal.

   This was a serious concern as the hydrated cement compounds probably do not contribute to strength gain and should thus not be used in predicting strength.

   It is accepted that the X-rays diffracted from hydrated cement compounds will not be diffracted at the same 2θ angles or inter-lattice spacings (crystalline identity) as the corresponding unhydrated cement compounds as the crystalline identity of the hydrated cement compounds do change during hydration.

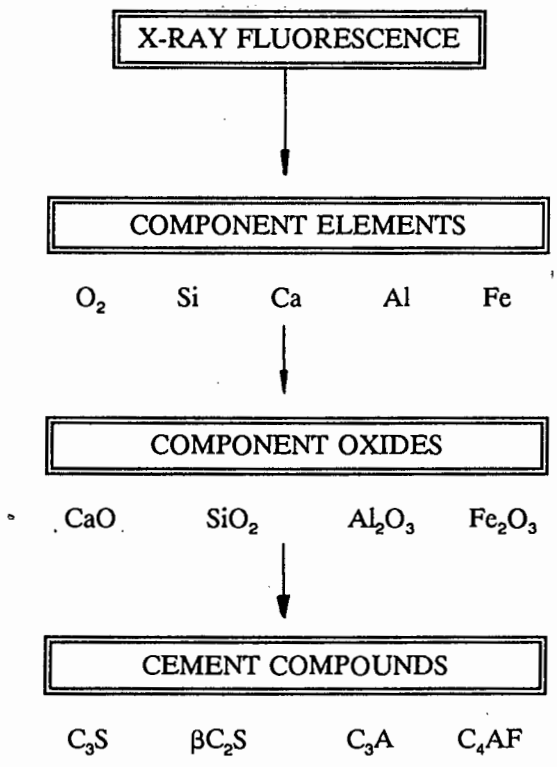
   The degree to which each crystal has hydrated can present a problem as the exterior of the crystal (which will hydrate first) will diffract the X-ray and it will not register as a relevant compound but, the interior of the crystal may still be unhydrated and may therefore still contribute to the strength gain of the cement. To simplify matters, the work on X-ray diffraction has been done assuming that all hydrated compounds in the cement do not have the same crystalline identity as the unhydrated compounds and that the hydrated compounds do not contribute to strength.

6.3 X-RAY FLUORESCENCE

An X-ray is an emission of photons from a material in an electronically excited state. For fluorescence to occur the electron in the higher-energy orbital must have the opposite spin orientation to the second electron in the lower orbital. These two electrons are said to be paired. X-ray fluorescence (XRF) is the emission which results from the return to the lower orbital of the paired electron[6.12].

XRF data is generally presented as spectra which are graphical representations of the fluorescence intensity versus wavelength (in nanometres). The amount of each element in a sample is determined using these spectra plots.

In cement chemistry, XRF is used in conjunction with the "Bogue" method to predict the potential chemical composition. This procedure is analysed as follows :



X-ray fluorescence uses X-rays to determine the amount of each element there is present in a sample. The Bogue method then combines the elements into compound oxides and cement compounds. This method is based on a few assumptions which is why the results of XRF analyses are referred to as the potential compound composition.

6.3.1 BOGUE ANALYSIS

The potential compound composition is calculated on the basis of the oxide composition of the cement.

The Bogue analysis is based on a cements' chemical composition consisting of pure forms of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). For reasons discussed in section 6.2.2 this assumption is not always true. The calculated composition therefore is referred to as a potential composition.

This calculation is often referred to as the Bogue composition after R.H.Bogue, the person who devised this method of calculation[6.13] :

$C_3S = 4.07CaO - (7.6SiO_2 + 6.7Al_2O_3 + 1.43Fe_2O_3)$

$C_2S = 8.60SiO_2 - 1.08Fe_2O_3 + 5.07Al_2O_3 - 3.07CaO$

$C_3A = 2.65Al_2O_3 - 1.692Fe_2O_3$

$C_4AF = 3.043Fe_2O_3$

The oxides CaO, SiO_2, Al_2O_3 and Fe_2O_3 represent the oxide contents as percentages by mass determined by X-ray fluorescence. The Bogue analysis has modifications for cements where the ferrite phase does not strictly conform to the classical compound C_4AF.

6.3.2 FACTORS INFLUENCING THE ACCURACY OF THE BOGUE ANALYSIS

The results of the Bogue analysis are generally inaccurate. The following factors should be taken into account when evaluating the accuracy of the results :

(a) The Bogue analysis assumes that the four major compounds have exact compositions. The formation of these compounds is based on the assumption that a condition of equilibrium had been reached during the reactions in the kiln. This is not absolutely correct as uncombined CaO left over in the kiln indicates that the reactions are incomplete and that total equilibrium had not been achieved. As pointed out by Lea[6.14], "..the content of the components calculated from the Bogue formula can be very far from the truth. The uncertainty in the Al_2O_3 : Fe_2O_3 ratio of the iron compound, and in the extent to which the clinker liquid has crystallised on cooling, account for these errors".

(b) Portland cement contains small amounts of other materials in variable quantities (eg. titania, magnesia and phosphate). These lesser compounds are not included in the Bogue analysis.

The manner of combination of the lesser compounds is not known. It may be possible that some of them, perhaps the alkalies, may have a significant influence on the relative amounts of the major compounds that are formed, but since the manner of their combination is not yet known the effects of their presence cannot be evaluated. Consequently, it is not possible at present to consider these compounds in the calculation[6.14].

(c) In South Africa the gypsum ($CaSO_4.2H_2O$) in Portland cement, which is added (to prevent "flash set"), is added after X-ray fluorescence of clinkers testing has been completed on the clinker samples. Thus, the gypsum does not complicate the determination of the potential compounds. But, for cements, the gypsum content must first be determined and then subtracted from the oxide results. The 5% filler (usually limestone in the Western Cape) should be taken into account when using the Bogue analysis.

6.4 COMPARISON BETWEEN THE XRD AND XRF METHODS

There are many differences between XRD and XRF :

a. XRF is an indirect method of analysis, it analyses intensity and the phases are determined by inference. Its results are influenced by the assumptions used in determining the combination of the elements to form compounds and what form the compounds should be in.

b. XRD is a direct quantitative method of analysis. It's main weakness is in the identification of the background for the integration of the peak areas but with standardization, this can be overcome .

6.5 CONCLUSIONS

From the literature review and the investigations conducted it can be concluded that :

1. The present method for predicting the compounds in cement in South Africa is a combination of X-ray fluorescence and the Bogue calculation. This method is an indirect method of analysis and it has built in errors due to the assumptions used in the formulation of the Bogue calculation.

2. X-ray diffraction is a direct method of analysis and although many difficulties are encountered in the analysis of cement, the method appears to be accurate to a few percent.

3. X-ray diffraction identifies the compounds by their diffraction patterns and determines the amount of each compound by integrating the area under the peaks.

4. The major compounds in Portland cement all exhibit diffraction peaks between the angular region from 28°2θ to 35°2θ. The diffraction peaks at the following 2θ angles 30.1, 31.1, 33.2 and 34.0 represent C_3S, C_2S, C_3A and C_4AF respectively.

5. The Bragg law is used to calculate the angle at which a diffracted X-ray would be "visible" when diffracted off a particular crystal. The Bragg law can also be used to calculate the interplanar spacing of the crystal lattice of a compound or element.

6. Preferential alignment of the crystals in a sample did not appear to have any significant effect on the intensity of the X-ray peaks, although it is possible that preferential alignment of the crystals may have been responsible for the slight fluctuations in the peak areas.

7. A change in the height of the sample surface tested would cause the X-ray intensity peak to shift to either the left or right of the predetermined position.

8. The grain size of the cement sample must be small enough for the absorption of X-rays to be negligible, but must be large enough to be representative of the powder as a whole.

9. The sample holders used during X-ray diffraction must be chosen so that they do not produce a peak at, or near the point where the compound peak analysis is to be done.

10. The general efficiency and alignment of the X-ray diffractometer should be checked before each series of samples is run. This can be done by running a standard stable substance (silicon) through the diffractometer and checking that the silicon peaks correspond to their specified points and heights.

11. Many methods exist to determine the phase composition. The four methods developed during this research were namely, the polynomial peak area and peak height methods as well as the straight line peak area and peak height methods.

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CHAPTER 7

THE EFFECT OF COMPOUND COMPOSITION ON COMPRESSIVE STRENGTH

7.1 INTRODUCTION

It has been established that the chemical composition of Portland cement is an important factor contributing to its compressive strength. In this chapter, the percentage of each individual major compound has been compared to the compressive strength and the effect each compound has, has been analysed.

The analysis between the strength and the compounds has been performed for individual compounds. The method of comparing the individual compounds to the strength has a built-in error because there is a certain degree of interaction between the compounds and they should be compared together.

7.2 THE EFFECT OF INDIVIDUAL MAJOR COMPOUNDS ON THE COMPRESSIVE STRENGTH USING SIMPLE LINEAR REGRESSION

The results of the X-ray diffraction analysis on the cement samples were imported onto a spreadsheet (Quattro Pro) and the peak heights and peak areas determined by the polynomial and straight line analysis methods (for the cements in Appendix 8) were compared with compressive strengths. The intensity of the diffracted X-ray (representing an amount of each compound) was compared with the compressive strength to determine whether a relationship between the two variables exists.

Each compound, from each sample was used in a regression analysis[7.3] in order to derive a linear relationship with the compressive strength as the dependent variable and the intensity for each compound as the independent variable.

The general formula for a straight line is:

$$Y = a + bX$$

When performing a regression analysis, the coefficients a and b must define the straight line which is most suited to describe the data.

The least squares regression method states that the sum of the squares of the differences between the observed values and the fitted line should be a minimum.

To justify the use of the regression analysis it must be shown that a significant relationship (correlation) exists between the variables. If all the data points lie close to the regression line, then the line is a good fit and accurate predictions can be expected. However, if the data is widely scattered, then the predictions will be inaccurate.

The degree of fit depends on the correlation between the two variables and is measured by the correlation coefficient[7.1].

$$\text{correlation coefficient (r)} = \frac{\sum XY}{\sqrt{\sum X^2 \sum Y^2}}$$

The correlation coefficient "r" always lies between +1 and -1. A positive correlation indicates a positive slope (ie. as X increases, Y increases) and a negative correlation indicates a negative slope (ie. as X increases, Y decreases). For perfect correlation r = +1 or -1 and for no correlation r = zero. If the calculated value of r is greater than the appropriate value in Appendix 5[7.1] then significant correlation has been established.

The graphs are based on a series of 22 sets of mortar cubes with each set comprising 5 cubes. The cubes were all tested after 27 days under water curing at 25°C. The curing also involved the rotation and mixing procedures mentioned earlier.

7.3 RESULTS

7.3.1 TRICALCIUM SILICATE

The graphs in Figures 24 to 27 represent the variation in 28 day compressive strength with respect to intensity (percentage) of tricalcium silicate for each sample measured using the polynomial peak height and area methods, the straight line peak height and area methods. At the 95 percent confidence level with a sample size of 22, with 21 degrees of freedom, for 2 variables, the critical tabulated correlation coefficient in Appendix 5 (95% confidence level) is 0,498. Since the tabulated correlation coefficient is greater than the experimental correlation coefficient, the "null hypothesis" is rejected. The correlation coefficients for the tricalcium silicate analysis vary from 0.53 to 0.666

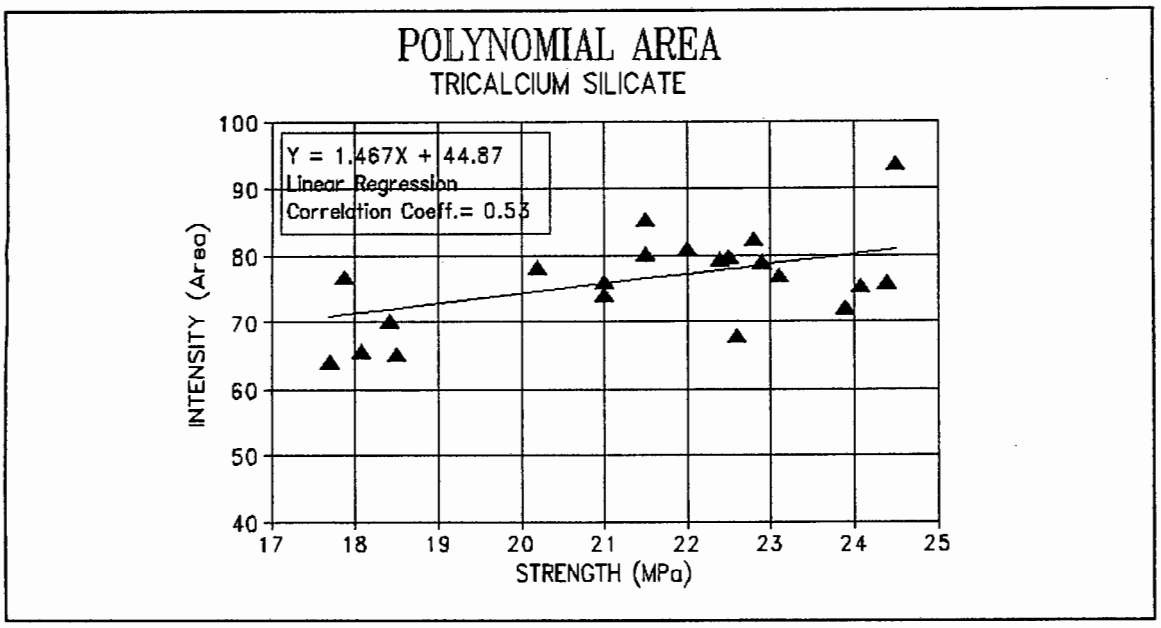

Figure 24 : Tricalcium silicate regression analysis by polynomial area

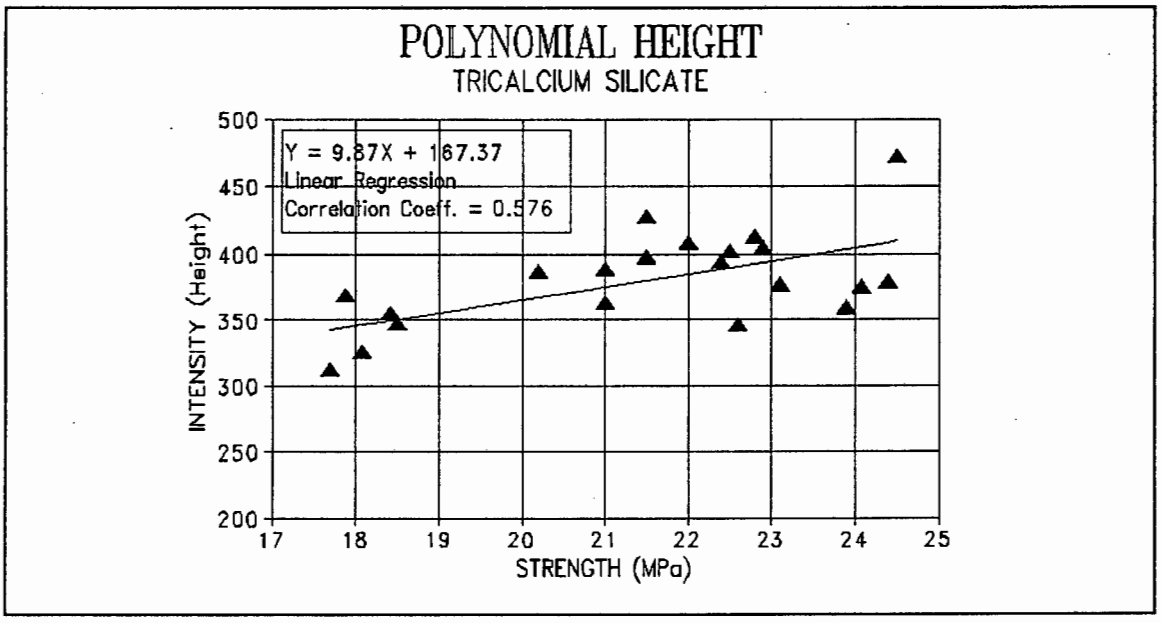

Figure 25 : Tricalcium silicate regression analysis by polynomial height

indicating that significant correlation, for this degree of freedom, has been established (see Appendix 5).

The graphs, which are a linear regression between the compressive strength (Appendix 8) of the samples and the intensity of the diffracted X-rays, show a trend indicating an increase in strength for an increase in the percentage tricalcium silicate in the cement for all four area calculation

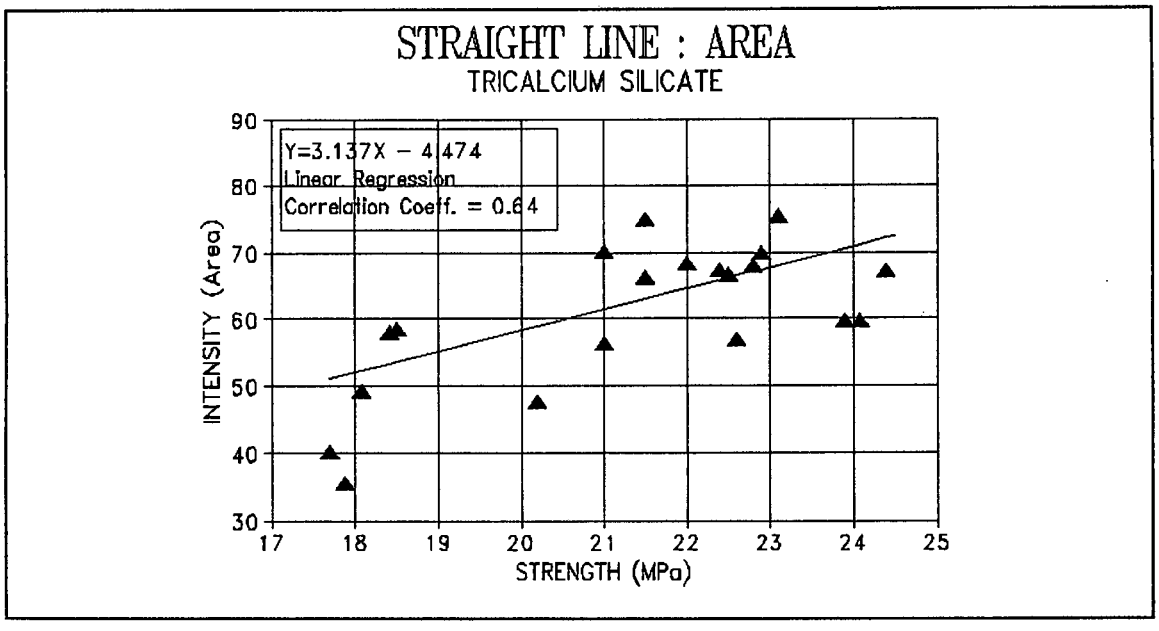

Figure 26 : Tricalcium silicate regression analysis by straight line area

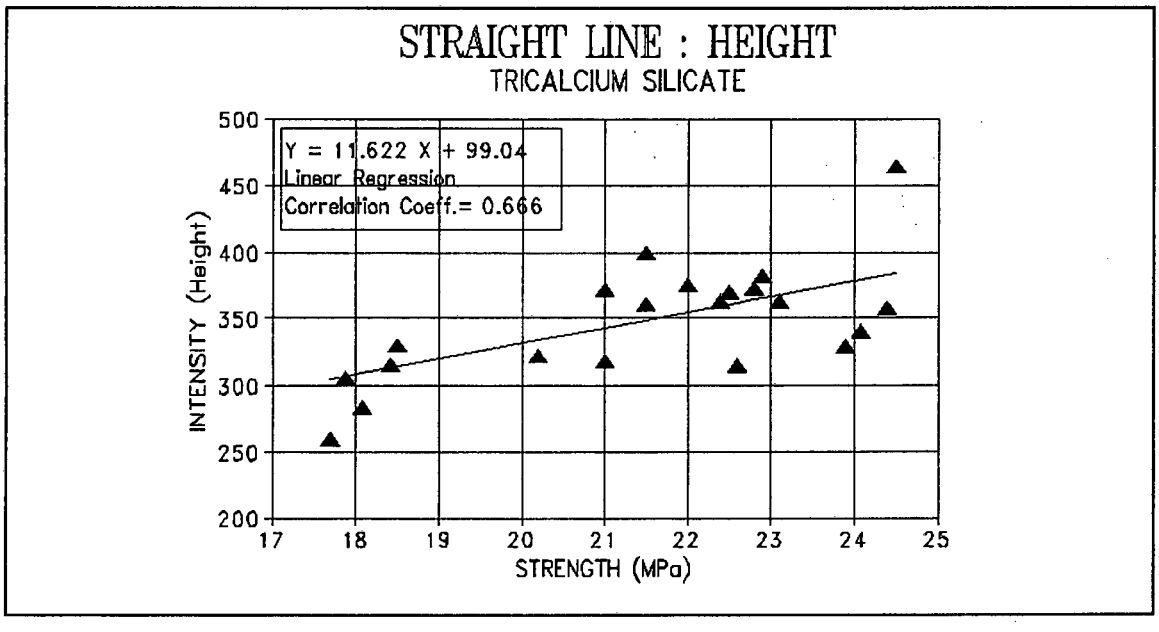

Figure 27 : Tricalcium silicate regression analysis by straight line height

methods. The increase in strength due to an increase in C_3S was expected as the literature is clearly in support of this fact[7.2, 7.3, 7.4, 7.5, 7.6].

The straight line height method of analysis indicated a better correlation and has thus been used further in this thesis for all the compounds although the results of the other methods (peak area, peak height and straight line area) are presented graphically in Appendix 6. In some of the other

compounds the straight line height method is not necessarily the better method but generally, where it does not have the higher correlation coefficient, the remaining methods also indicate poor correlation.

7.3.2 DICALCIUM SILICATE

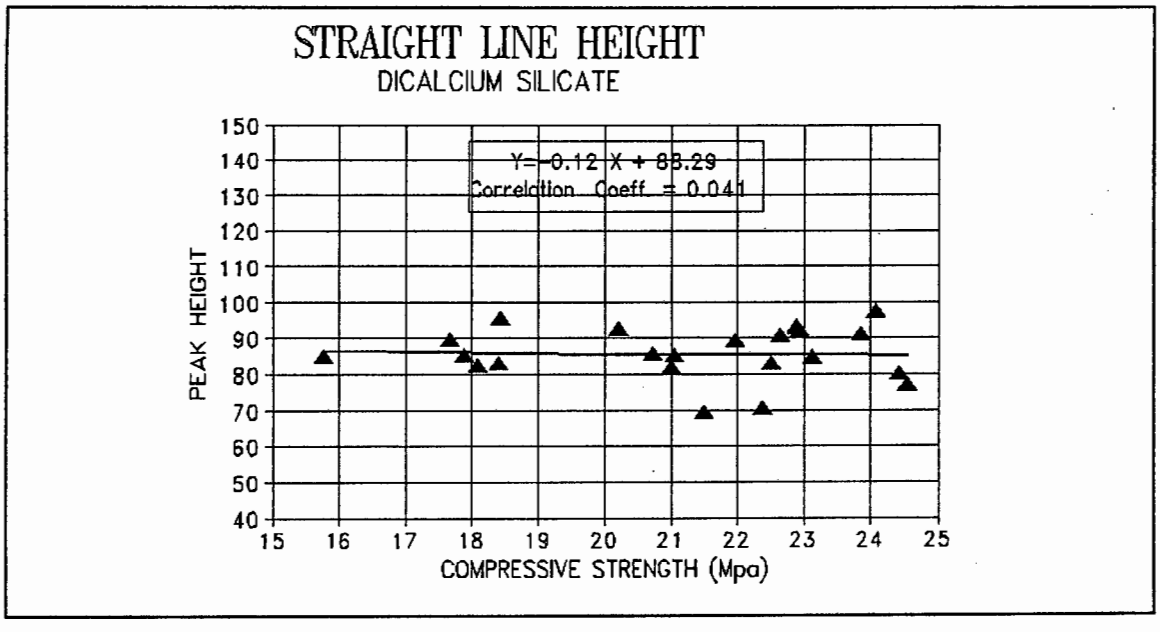

Figure 28 :Dicalcium silicate regression analysis by straight line height

The dicalcium silicate (C_2S) single regression analysis in Figure 28 indicates that dicalcium silicate does not effect the strength of mortar at 28 days. The minimum correlation coefficient for there to be significant correlation is 0.498 (Appendix 5) The correlation between the strength and the peak height for C_2S is very poor (0.041) indicating that there is virtually no correlation between C_2S and strength. This result corresponds to Fulton [7.3] and other literature[7.7, 7.8, 7.9, 7.10]. According to Blaine et al[7.11] the dicalcium silicate content only has a positive influence on strength at 5 and 10 years. This corresponds to the above result although the time period (5 to 10 years) contradicts the previously listed references which generally refer to C_2S as having a beneficial effect on strength after a period of approximately 1 month.

7.3.3 TRICALCIUM ALUMINATE

The regression analysis examining the relationship between tricalcium aluminate to compressive strength in Figure 29 indicates a low correlation of 0.2 between the two variables. According to Appendix 5, a correlation coefficient of 0.2 is a "poor" correlation and indicates that there is little

or no relationship between the two variables. This may be due to the cement used for the data in Figure 29, marketed as OPC, only having between 2% and 4.5% C_3A in comparison to the usual 5% to 12%.

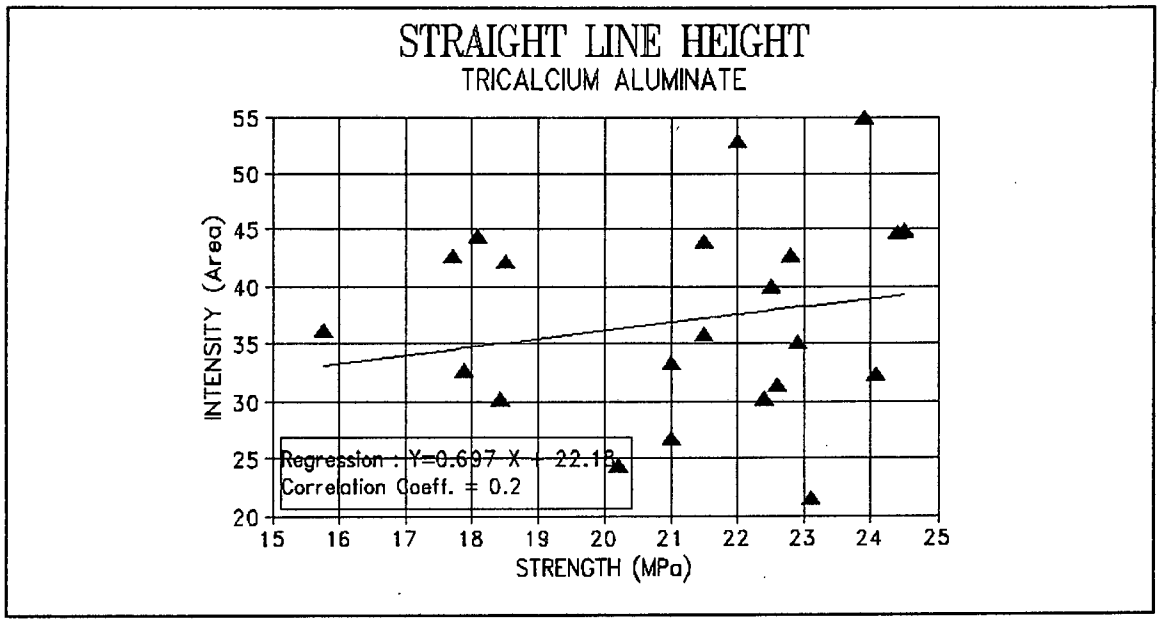

Figure 29 : Tricalcium aluminate regression analysis by straight line height.

There are two possible reasons why the C_3A had little effect on the compressive strength :

1. The C_3A content was so low that it had no detectable effect on the hydration and development of the strength of the cement.

2. The low C_3A content resulted in its contribution to the strength of the cement being overshadowed by the other more predominant compounds.

7.3.4 TETRACALCIUM ALUMINOFERRITE (C_4AF)

Figure 30 indicates that as the percentage of C_4AF decreases, so the strength increases. The results in figure 30 indicate a "poor" correlation between the level of C_4AF and strength but this conclusion should be carefully considered as certain authors propose that C_4AF has no strength related properties[7.12] while others feel that C_4AF contributes positively to strength[7.6].

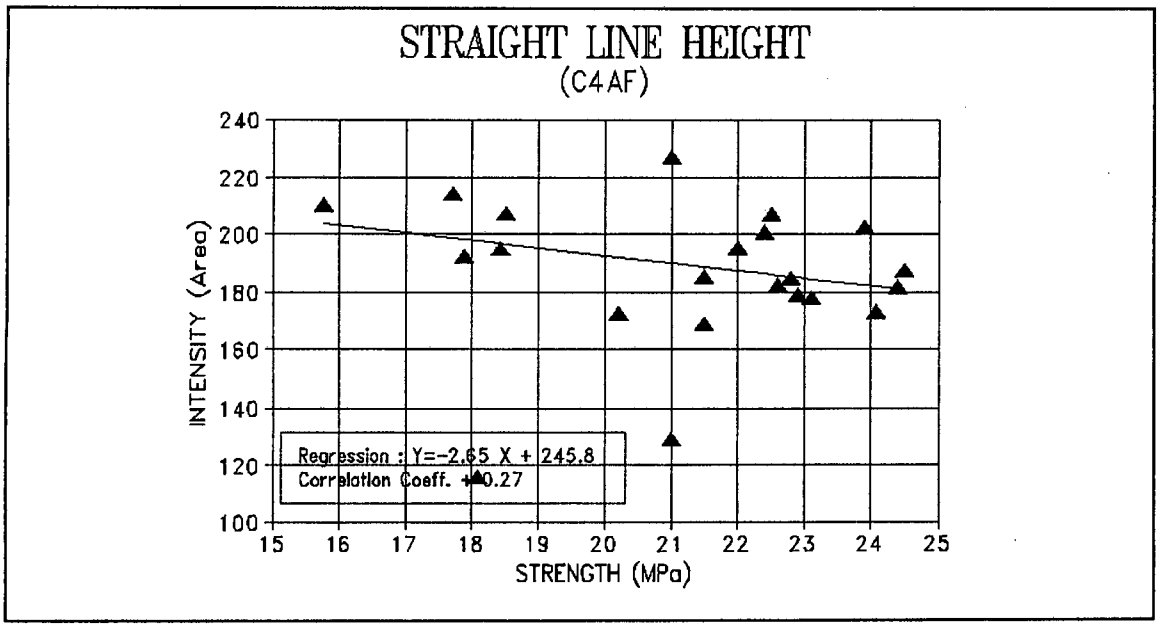

Figure 30 : Tetracalcium aluminoferrite regression analysis by straight line height.

The amount of C_4AF present is minimal and the decrease in C_4AF represents an increase in another compound. Considering the correlation of the graph for C_4AF, the single regression coefficient indicates that C_4AF has no relationship to the compressive strength of hardened cement.

7.4 EVALUATION OF THE CORRELATION COEFFICIENTS

The correlation coefficients for the single regression analyses, performed on the XRD intensity of each major compound and the strength of the mortar cubes, indicated that tricalcium silicate was the only major compound with significant correlation (0.666). The correlation coefficients of dicalcium silicate (0.041), tricalcium aluminate (0.20) and tetracalcium aluminoferrite (0.27) all indicated that little or no relationship exists between the amount of each compound in the cement (intensity) and the compressive strength.

TABLE 13 : MAJOR COMPOUND CORRELATION COEFFICIENTS

MAJOR COMPOUND	CORRELATION COEFFICIENT	DEGREE OF CORRELATION
C_3S	0.666	SIGNIFICANT
C_2S	0.041	NONE
C_3A	0.20	LOW
C_4AF	0.27	LOW

Although this result is significant, the dependant variable (compressive strength) depends on more than one independent variable at the same time and the prediction of the dependant variable can be improved by a multiple regression analysis for the following reason :

> The difference between the simple and multiple regression methods is that a multiple regression establishes the effect of each independent variable with the other independent variables kept constant, whereas a simple regression does not control the other independent variables.

7.5 CONCLUSIONS

The results of the single regression analysis appear to indicate that :

1. Tricalcium silicate (C_3S) has a major effect on the compressive strength. An increase in C_3S corresponds to an increase in strength.

2. Dicalcium silicate (C_2S) has a poor correlation with the compressive strength and does not appear to affect the compressive strength for the initial 28 day curing period.

3. Tetracalcium aluminoferrite (C_4AF) does not appear to influence the compressive strength. It's correlation to strength is "poor". This finding is supported by many authors[7.2, 7.4, 7.5, 7.6].

The results of the simple regression analysis indicate that relationships exist between certain of the major compounds and the compressive strength. The relationships may be inter-related preventing the simple regression analysis from indicating their true relationships. The relationship between the major compounds and compressive strength should therefore be determined using a multiple-regression analysis.

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CHAPTER 8

THE EFFECT OF THE FINENESS OF CEMENT ON COMPRESSIVE STRENGTH

8.1 INTRODUCTION

A factor which affects the potential strength of cement is the fineness to which the cement particles are ground. The finer the cement, the greater the total surface area of the particles becomes. The rate of hydration of cement increases as its surface area increases causing an increase in the rate of gain of compressive strength. This occurs because a larger surface area is available for hydration.

Cement particles are usually graded within sizes varying from about 1 to about 200 μm. In South Africa, the "fineness" of cement is determined using the modified Blaine air permeability test described in SABS 471-1971[8.1]. This method is very similar to the Lea and Nurse test described in BS 12-1971[8.2]. In the United States the standard method for "fineness" determination is the Wagner Turbidimeter[8.3].

The modified Blaine and the Lea and Nurse tests for air permeability is a measurement of the specific surface area and is a number describing the total surface area of particles in a gramme of cement, expressed as cm^2/g. While the surface area as measured by air permeability methods is a valuable index of the fineness of a cement, it does not provide precise information regarding the distribution of particle sizes. A specific surface area can represent widely different gradings.

The most complete information regarding cement fineness can be obtained using the particle size distribution. The particle size distribution can be determined using either a laser diffraction spectrometer, the sedimentation rate measurement, microscopic sizing using average dimensions (calculated by direct measurement) or by elutriation. The elutriation method is based on the dependence of the rate of free fall of particles on their diameter.

The oldest and simplest method however, is to sieve a cement sample through fine sieves and record as a percentage the amount retained by each sieve (ASTM C 184-74). Unfortunately, this test provides little information about the quantity of the most important cement particles, namely, those that are smaller than ≈50μm and has therefore been dropped from the ASTM tests.

The fineness of grinding of cement has an effect on several technically important properties of concrete and mortar. All factors remaining constant, a finer cement will affect concrete or mortar in the following

ways :

(i) The permeability will be reduced since the hydrated paste will be more dense.

(ii) The rate of heat generation will increase during the early stages. This is of importance in large mass concrete structures.

(iii) The bleeding of the mix will be reduced because of the increase in the specific surface area.

(iv) The time to initial and final set of the concrete/mortar will be reduced.

(v) The larger surface area will cause higher earlier strengths. This is due to the increased surface area of the cement particles available to react with the water causing a more rapid formation of gel. At later ages this strength premium may be barely noticeable.

(vi) A finer cement, when in mortar or concrete, tends to cause a higher water demand. This tends to increase the overall cost of producing a concrete for a certain workability. The increase in the water content would also tend to increase the shrinkage.

In this investigation, clinker (with the usual addition of gypsum and limestone) was ground to different finenesses, the particle size distribution was determined and conclusions were drawn from the compressive tests performed on mortar made with this cement.

8.2 METHOD OF GRINDING

To prevent the partial hydration of the clinker a sample was taken after clinkering and before storage. The clinker and gypsum were crushed at the University of Cape Town from their original coarse size immediately prior to milling to sizes suitable for use in concrete. The clinker and gypsum (hereafter called the constituents) were ground to various finenesses such that the particle size distributions of the constituents ranged from very coarse to very fine (Figure 31).

The grinding of the gypsum and clinker was performed in three stages. Firstly, the constituents were individually broken up in a jaw crusher to approximately 5mm in diameter. Secondly, the output from the jaw crusher was fed into a disc pulveriser which further reduced the clinker and gypsum to sizes below 1mm in diameter. The constituents were then dried at 100°C to remove any moisture and prevent a "balling" effect

of the fine particles in the mill[8.9].

The drying temperature of 100°C was not sufficient to drive off the bonded water in the gypsum (calcium sulphate di-hydrate → $CaSO_4.2H_2O$). This water will only be driven off at a temperature of 160°C.

Finally, the clinker and 4.5% gypsum was placed in the ball mill and milled to various finenesses. The limestone which would normally be added to OPC was not added to the constituents as it serves no purpose in the cement except to act as a filler and grinding aid. The ball mill ground the clinker and gypsum to particle sizes which ranged from 1μm to ≈200μm as seen in Figure 31.

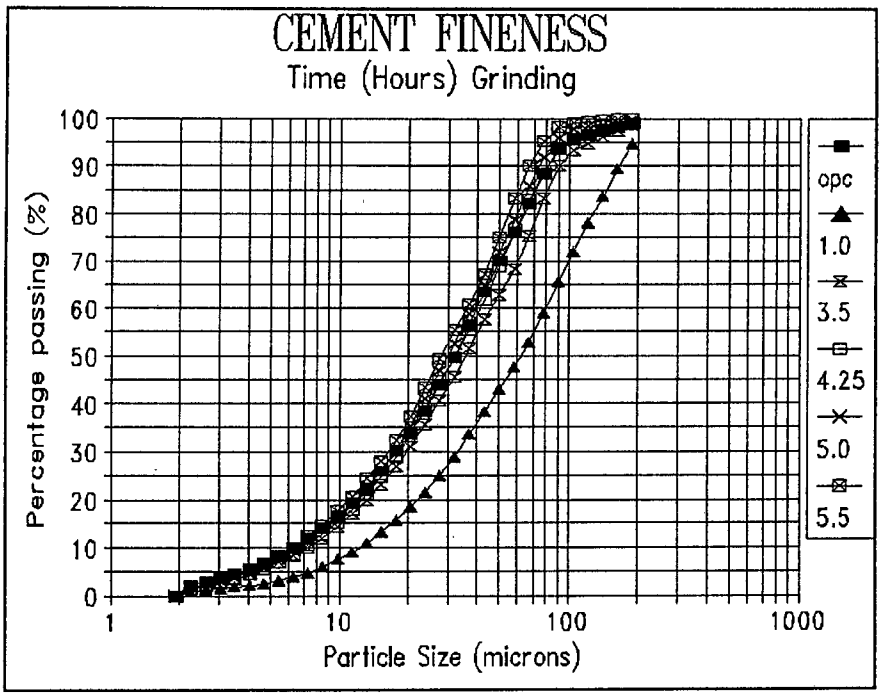

Figure 31 : Fineness grading of cement particles for various grinding times

8.3 PARTICLE SIZE DETERMINATION

The particle size of cement has been described and tested in many ways. The Blaine test does not indicate what percentage coarse, medium or fine cement exists. It has been shown by Lochner[8.4] that distinct variations in strength can be obtained from cements with the same specific surface area but where the particle size distributions of the cement differ. Also, Popovics[8.5] has shown that cement of a certain size grading develops lower strengths at later ages than the same cement with an identical specific surface area but which contains finer and coarser particles.

In the Blaine test a cement sample of about 28g is compacted into a cell to a porosity of 50%. Then, a known volume of air is passed through the compacted sample at a prescribed average pressure, with the rate of flow diminishing steadily. The time for the flow to take place is measured and is converted to the specific surface area.

Particle size distribution can be measured using a laser diffraction spectrometer (LDS). The LDS consists of optical particle counters in which the particles pass successively into a measuring cell and emit a scattered light pulse affecting a change in transmission, the extent of which depends on the particle size[8.6]. The LDS on which this research has been based was a Malvern particle sizer. The curves from the LDS show a 95% reproducibility confidence level, calculated from seven measurements[8.6]. The results of the particle size distribution analysis performed with the LDS are attached in Appendix 10.

The dispersant used to test the cement was water. Other dispersants such as a non-polar liquids (paraffin) could also have been used but the system (used by many other researchers) was set up for a water dispersant. The cement was vigorously mixed in a mixing tank prior to testing. As the cement was only a few days old and the duration of the test was approximately 1 minute, the influence that hydration would have on the results were minimal.

8.4 MIXING, CASTING AND CURING

The mortar used for relating strength to the fineness was a mixture of Portland cement, water and Klipheuwel sand. The mortar was mixed in the following proportions :

TABLE 14 : MORTAR MIX PROPORTIONS

CEMENT	SAND	WATER
1	2.5	0.65

*measured by mass

The mortar was mixed in the standard manner used during this research, siphoned into the mortar cubes, vibrated for one minute and then rotated at 3.5 rev/min to prevent bleeding. The cubes were stripped the following day, cured under water at 25°C for 27 days and crushed on the 28th day.

8.5 THE EFFECT OF FINENESS ON BLEEDING

The clinkers ground to different ranges of fineness conformed to Higginson's[8.7] results, with diminishing effect as the surface area (Blaine) increased above 4300cm^2/g. The clinker which was coarsely ground to

abnormally low fineness (ie. Blaine surface area $<1500cm^2/g$) did not behave as expected as bleeding was reduced. The reduction in bleeding in this coarse region was unexpected as the standard explanation for a reduction in bleeding is an increase in the specific surface area of the mix constituents. The degree of bleeding was measured using the pipette method (ASTM C232-171[8.8]).

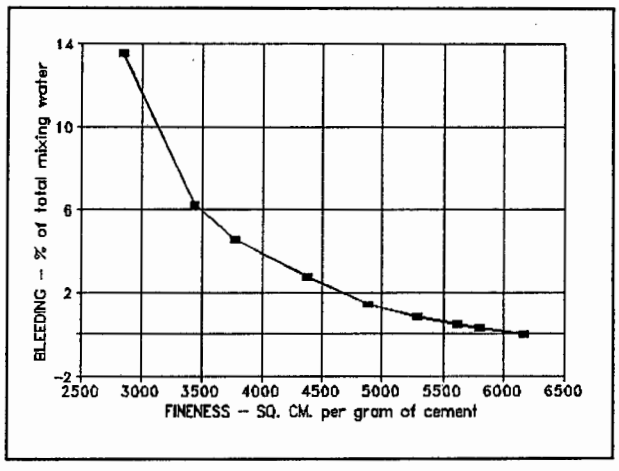

Figure 32 : The effect of cement fineness on the bleeding of concrete[8.7]

Possible reasons for the reduction in bleeding of the very coarse cements are as follows :

1. Cement particles are angular, elongated and in a very coarse sample may be sufficiently large enough to cause inter-locking of both the fine aggregate and the cement particles. The inter-locking of the particles would tend to prevent sedimentation and thus, bleeding.

2. The cement lacks sufficient fines causing large voids. Internally, these voids hold the water leaving little water for bleeding but, depending on the degree of coarseness, external bleeding (along the shutter surfaces) may also occur.

The bleeding of mortar/concrete is reduced with finer cements. The results of tests conducted by the Bureau of Reclamation[8.7] showed a direct relationship between the bleeding of concrete and the fineness of cement. Figure 32[8.7] indicates the amount of bleeding for various cements with different finenesses.

8.6 PARTICLE SIZE ANALYSIS

Certain particle sizes have an adverse effect with respect to the compressive strength of mortar and concrete and others have a beneficial effect. The particle size distribution was divided into many bands and compared to the compressive strength of cast samples of cement mortar. A regression analysis was performed and the size limits of the bands were changed until the particles which affected the compressive strength were identified.

The reason that the different particle size bands have different influences on the strength of the cement mortar can be speculated upon. Firstly, the increase in strength associated with finer cements may be due

to the reduced amount of coarse particles in the cement, or because certain combinations of finer and coarser cement particles may optimise the rheological properties of the cement paste. Secondly, the effect that each particle size band has on strength may differ because the size of the particles will determine the degree of hydration of the cement particles at any particular age (Figure 33).

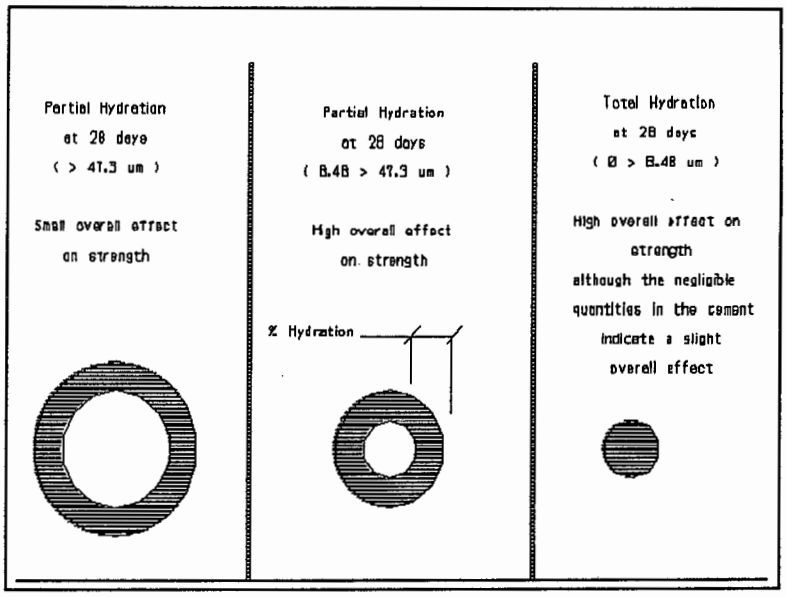

Figure 33 : Pictorial representation of the hydration of cement particles

A second series of tests was run to determine how the compressive strength was affected when large variations in the particle size distribution occurred. To obtain cements with large variations in the particle size distribution the clinker was ground to very different artificial limits before being tested.

8.7 DISCUSSION OF RESULTS

The compressive strengths of the cement mortar cubes at 28 days were compared to the percentage particles in 5 selected particle size bands. A regression analysis was performed using the percentage particles in each band and the compressive strength of the mortar cubes. The results of the regression analysis in Figure 34 indicate that the particles smaller than ≈8.48μm and between the sizes ≈47.3μm and ≈57.3μm had no significant contribution to the compressive strength. The particle sizes larger than ≈57.3μm had an apparently negative contribution to the strength and the particles between ≈8.48μm and ≈47.3μm had a strongly positive contribution to strength. The particle size bands were chosen by analysing small size bands and combining the bands to form groups with either high or low influences on the compressive strength.

This result simply means that the strength of cement mortar increases most with an increase in the number of particles within the size band 8.48μm to 47.3μm. The cement particles greater than ≈47.3μm have a small overall effect on strength for the following reasons :

1. The cement particles in this size range may only achieve partial hydration at 28 days (Figure 33).

2. The surface area of the cement available for hydration is drastically reduced.

An increase in the number of particles in the coarse band results in a decrease in the more active particles in the medium band resulting in a net strength loss.

The coarse particles are useful for continued strength gain after 28 days as these size fractions might not have achieved full hydration at 28 days and, with sufficient curing, may play a role in the further strength development of the cement.

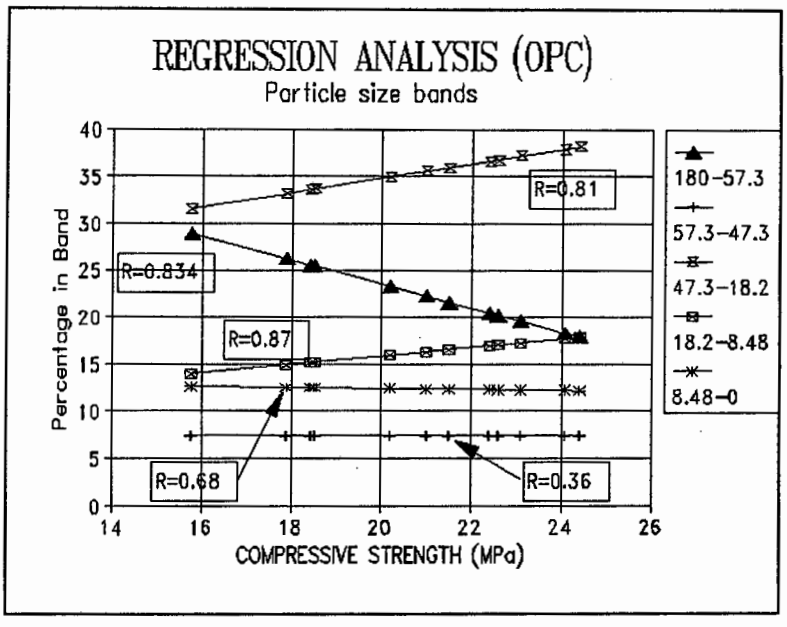

Figure 34 : A regression analysis comparing particle size bands to compressive strength. **Note - the band sizes (eg 180 - 57.3) are in microns.**

The fineness data used in Figure 34 is attached in Appendix 10.

In sorting cement particle sizes into those that contribute to the 28 day strength and those that don't, Popovics[8.5] is of the opinion that it is possible to substitute the extreme particle size ranges (>47.3 microns and <8.48 microns) with less expensive, suitable, inert particles, such as limestone particles, without damaging the strength development up to 28 days.

8.8 CONCLUSIONS

The fineness of the cement particles has a critical influence on the properties of hardened cement paste. The fineness not only affects the permeability, rate of heat generation, water demand, bleeding and durability, but it also influences the compressive strength. The fineness influences the compressive strength mostly with respect to the surface area available for hydration.

The compressive strength at 28 days is therefore mostly influenced by the percentage of particles within the size band 47.3μm to 8.48μm. The particles greater than 47.3μm appear to have little overall effect on the compressive strength and the particles smaller than 8.48μm do not seem to influence the compressive strength at all.

The fineness of cement has an effect on the compressive strength and should therefore be included in a multiple regression analysis along with the major chemical compounds in order to determine the absolute contribution that fineness contributes to strength. For this purpose, fineness is arbitrarily defined as the percentage of the cement particles (by mass) which lie in the particle size band 47.3μm to 8.48μm.

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CHAPTER 9

STRENGTH PREDICTION OF CEMENT MORTAR

9.1 INTRODUCTION

It has been established that the chemical composition and cement fineness affect the compressive strength of cement mortar most, other aspects being equal. The effect of the chemical composition on the 28 day compressive strength of cement mortar appears to be mostly dependant on the tricalcium silicate content of the cement and the fineness of the cement appears to have a positive contribution to the strength of cement when the percentage particles within the size range 8μm to 49μm increases.

The results obtained from the previous simple regression analyses indicate that strength and compound composition are related but as the strength (as dependant variable), may depend on more than only the two factors mentioned above and because these factors may influence each other, all the possible contributing factors have to be combined in a multiple regression analysis.

The multiple regression analysis establishes the effect of each independent variable while the other independent variables are effectively kept constant. The work in this chapter was performed in conjunction with Professor T.T. Dunne[9.1] of the Department of Statistical Science at the University of Cape Town.

A suggested approach to analysing the strength in terms of the chemical compound composition and fineness is to fit a linear equation of the form :

$$\text{Strength} = a + b(C_3S) + c(C_2S) + d(C_3A) + e(C_4AF) + f(\text{Fineness})$$

where the symbols in brackets represent the percentage by weight of the compounds, and a, b, etc., are constant parameters representing the contribution of one percent of the corresponding compound to the strength of the cement paste.

It is surmised that this form of equation can be used for strength predictions[9.2].

This is not an entirely new concept and many investigators have attempted to formulate these effects. Neville[9.3] believes it is possible to predict the strength of cement on the basis of its compound composition. This would be in the form of a formula of the type :

$$\text{Strength} = a.(C_3S) + b.(C_2S) + c.(C_3A) + d.(C_4AF)$$

Alexander[9.4] also believes that compressive strength can be related as follows :

$$CS = b_o + b_1(C_3S) + b_2(\text{Alum}) + b_3(\text{Sp-s})$$

CS	=	Compressive strength
C_3S	=	Tricalcium silicate content of the cement
Alum	=	Aluminate content of the cement
Sp-s	=	Specific surface area of the cement
b	=	Factors

In this chapter, the effect of each compound and the fineness of the cement is examined together with respect to strength, constants are derived to fit each contribution and a model is proposed for strength prediction. Finally, the limitations of the model are discussed.

9.2 DATA MANIPULATION

The results of the X-ray diffraction analysis on the cements tested were changed from an intensity of X-ray received to a percentage of the total amount of each compound in the sample.

As no standard samples were available to calibrate the X-ray diffractometer, for each particular compound, the intensities were proportionately changed to percentages by equating the average intensity, for the range of cements tested, found for that compound, to the percentage of that compound normally present in Ordinary Portland cement in the Western Cape. The intensities were changed in the following ratios :

TABLE 15 : THE ASSUMED RELATIONSHIP BETWEEN THE X-RAY DIFFRACTION INTENSITY AND THE PERCENTAGE OF THE COMPOUND PRESENT IN THE CEMENT

COMPOUND	INTENSITY	PERCENTAGE
C_3S	259.67	44.16
C_2S	89.63	39.16
C_3A	42.64	3.75
C_4AF	214.13	12.93

The data had to be changed to percentages because X-ray intensities did not relate directly to the total amount of each compound in the cement. This transformation was not a problem previously as each compound was dealt with separately and no inter-relationships between the individual compounds were dealt with.

The results of this analysis will therefore not be precise as the amount of each compound in the cement used for this analysis was transformed using the assumed ratios in Table 15. This can be corrected by calibrating the X-ray diffractometer used for this research. The calibration can be done by running a pure sample of each compound (at exorbitant cost) through the diffractometer and analysing the peaks for that compound in the manner used so far. The calculated peak will then represent 100% of that compound and the data used for the multiple regression analysis can then be adapted accordingly, by means of the values in Table 15. These results show the change from the diffractometer intensity to a percentage of each compound and will enable the system to be calibrated should pure compounds be made available for XRD work.

9.3 MULTIPLE REGRESSION ANALYSIS

The general case for a relation between the dependent (response) variable y and the independent (exploratory) variables $x_1, x_2 \ldots\ldots x_k$ can be expressed as[9.4] :

$$y = b_0 + b_1x_1 + b_2x_2 + \ldots\ldots b_kx_k$$

Where b_0 is a constant and $b_1, b_2 \ldots\ldots b_k$ are partial regression coefficients. The variables denoted by the letter x need not be linear and the model admits the form :

$$y = b_o + b_1 x_1^a + b_2 x_2^b + \ldots\ldots b_k x_k^c$$

However, the linear condition makes it easy to apply the principle of least squares in order to yield the standard error for prediction.

The multiple regression correlation coefficient, ρ, measures the degree of association between the dependent variable and all the independent variables taken together.

The variables and their respective values used in the multiple regression analysis are listed in Appendix 8 and the relevant statistical data is summarised in Table 16 below.

TABLE 16 : GENERATED STATISTICAL DATA

VARIABLE	MEAN	STANDARD DEVIATION	COEFF. OF VARIATION	MINIMUM	MAXIMUM
C_2S	33.55 %	3.537 %	0.105	25.87 %	38.51 %
C_3A	2.945 %	0.688 %	0.234	1.681 %	4.221 %
C_3S	52.27 %	3.704 %	0.071	43.42 %	60.74 %
C_4AF	10.01 %	1.307 %	0.131	7.34 %	12.71 %
STRENGTH	21.18MPa	2.506 MPa	0.118	15.76 MPa	24.54 MPa
FINENESS	54.94 %	4.915 %	0.089	46.70 %	63.29 %

The standard deviation is the square root of the observed variance and the coefficient of variation is the standard deviation divided by the mean of the population.

A multiple regression analysis was performed for three cases. The first case dealt with four variables, namely, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and the fineness of the cement. The second case dealt with the same variables except that tetracalcium aluminoferrite (C_4AF) was substituted for C_2S and the final case dealt with C_3S and the cement fineness only.

9.4 SIGNIFICANCE OF MULTIPLE REGRESSION

To test whether a regression analysis or the observed differences is due to chance only, or whether the difference can be considered statistically significant, the "principle of hypothesis testing" must be applied. A hypothesis test compares the means of samples as a method of determining statistical significance.

A hypothesis is only an assertion which is subject to verification. The principle of "null" hypothesis testing is to examine the assumption that any observed difference between two population parameters is only due to random sampling errors. The null hypothesis claims that an observed distribution or set of data does not differ significantly from a null version of an assumed model (regression equation but with all b_i values set to zero). In the null model the probability of variation in the data, due to chance alone, is measured and if the probability is very small the null hypothesis is rejected and one infers that there is a real relationship (ie. it is presumed that the model has some predictive powers and that one or more of the b-values are non-zero). The null hypothesis is rejected if the proportional areas under two tails (Figure 35) is smaller than that corresponding to the specific level of significance, which is when the absolute value of the calculated statistic is greater than the tabulated statistic (Appendix 5).

There is no statistical test capable of providing complete certainty. Judgement should be exercised in interpreting the results as there are many practical reasons why the statistical test of hypothesis cannot be taken as fact. However, the statistical hypothesis test approach is the only method available whereby some degree of reliability can be determined.

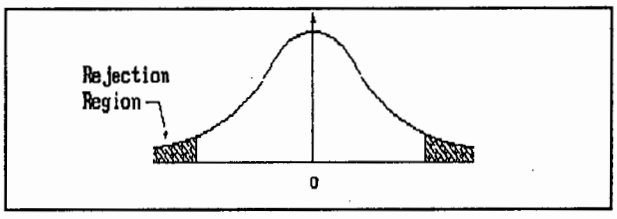

Figure 35 : The tail area for a two sided normal distribution

9.4.1 THE *T* STATISTIC

The t test is applicable to samples drawn from normally distributed data and is a comparison between the means of two random sized samples. Since the null hypothesis is examined by the t test, to be consistent with the hypothesis, the variances of two samples must not be significantly different.

Since in a given linear model one or more of the included variables may be either independent or of little consequence, it is important to check each variable in a model with a view to eliminating it if there is evidence to suggest that it has little marginal usefulness. The t-statistic for these variables is appropriate, and is equivalent to a special type of *F*-statistic.

The null hypothesis is rejected at a 5 percent level of significance. If the calculated t is greater than the tabulated value (Appendix 5) at the specified level of significance, the null hypothesis is rejected and the difference is concluded as being significant. If the calculated t is not greater than the tabulated t at the 5 percent level of significance, then the null hypothesis is accepted.

9.4.2 THE F-STATISTIC

Every submodel of a linear model can be used to generate an *F*-statistic. Large statistics for a specified sub-model indicate that the sub-model in question is a statistically significant component of the linear model under review, and should be retained.

9.4.3 THE P-VALUE

The p-value is a term which examines the relevance of a variable in a multiple regression analysis. As the p-value tends to zero, the importance of the variable increases and likewise, as the value tends to 1, the variable becomes less important. The p-value is only an indication by which certain variables can be said to be relatively unimportant to the predictive powers of a regression equation.

9.5 DISCUSSION OF RESULTS

The three cases analysed by multiple regression indicate which major compounds are insignificant with respect to compressive strength (in MPa) at 28 days of 100mm mortar cubes, tested in the standard manner.

The three statistical values, namely the T-statistic, F-statistic and the P value have been used to identify the significant compounds (with respect to compressive strength).

9.5.1 MULTIPLE REGRESSION CASE 1

Four values were used in this multiple regression case. The four compounds used were C_2S, C_3A, C_3S and the fineness of the cement (size range 8.48 to 47.3μm).

In Table 17, as the P value tends to zero, the significance of the compound increases.

TABLE 17 : ANALYSIS OF VARIANCE : CASE 1

VARIABLE	STD. ERROR	t	P-Value
C_2S	0.2439	-0.12	0.90
C_3A	0.6403	-0.40	0.69
C_3S	0.2499	0.91	0.37
FINENESS	0.09	3.15	0.01

The degrees of freedom within regression case 1 indicate that a minimum t-value of 2.96 is necessary for any variable to enable the null hypothesis (of its redundancy) to be rejected. The variables C_2S, C_3A and C_3S therefore failed this test and according to the p-values of each of these variables only the fineness appeared significant ($p < 0.01$).

The t-value was lowest for the C_2S and C_3A variables implying that at least one of them should not be included in the regression analysis as their effects are not significant.

TABLE 18 : F-STATISTIC : CASE 1

	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F-STATISTIC
REGRESSION	77.2648	4	19.3162	6.01
RESIDUAL	56.6388	17	3.2140	

The regression analysed in case 1 explains 57.7% of the total sum of the squares. The unexplained variations therefore amount to 42.23%. The *F*-statistic ratio indicates that there is a relationship

between the variables taken as a group and the compressive strength. The relationship computed from case 1 is :

$$\text{Strength} = -4.57 - 0.030(C_2S) - 0.257(C_3A) + 0.257(C_3S) + 0.284(\text{Fineness})$$

9.5.2 MULTIPLE REGRESSION CASE 2

The four compounds used in this multiple regression case were changed to C_3A, C_3S, C_4AF and the fineness of the cement. C_2S was left out as case 1 indicated that C_2S did not have a significant influence on the compressive strength. C_4AF was included as, even though it should not exhibit much influence on the compressive strength, it was necessary to examine its influence.

TABLE 19 : ANALYSIS OF VARIANCE : CASE 2

VARIABLE	STD. ERROR	t	P-Value
C_3A	0.5954	-0.37	0.72
C_3S	0.1264	2.07	0.05
C_4AF	0.3621	0.10	0.92
FINENESS	0.09	3.14	0.01

Of the variables in this regression analysis (Table 19), both C_3A and C_4AF have high standard errors and low t-statistics. The p-values for C_3A and C_4AF are 0.72 and 0.92 respectively. This means that the null hypothesis for C_3A and C_4AF may well be unusable, and the variables could be omitted.

C_3S has a t-value sufficient to reject the null hypothesis and it must therefore be included in the model. The fineness also exceeds the value necessary to reject the null hypothesis and is also included.

TABLE 20 : F-STATISTIC : CASE 2

	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F-Statistic
REGRESSION	77.2511	4	19.3128	6.007
RESIDUAL	54.6526	17	3.2149	

The regression explains 58.56% (sum of squares) of the variations in strength. The unexplained variations amount to 41.43%. The relationship between the variables and compressive strength computed from case 2 is :

$$\textbf{Strength} = -7.765 - 0.219(C_3A) + 0.261(C_3S) + 0.038(C_4AF) + 0.283(\text{Fineness})$$

9.5.3 MULTIPLE REGRESSION CASE 3

The multiple regression cases 1 and 2 have shown that the compounds C_2S, C_3A and C_4AF do not have any significant influence on the compressive strength.

TABLE 21 : ANALYSIS OF VARIANCE : CASE 3

VARIABLE	STD. ERROR	t	P-Value
C_3S	0.1062	2.51	0.02
FINENESS	0.0800	3.42	0.00

Only two variables were used in this regression analysis. Both the variables (C_3S and the fineness of the cement) had very small standard errors.

TABLE 22 : F-STATISTIC : CASE 3

	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F-Statistic
REGRESSION	76.7455	2	38.3728	13.218
RESIDUAL	55.1582	19	2.9031	

The exclusion of C_2S, C_3A and C_4AF appears to have had no effect on the accuracy of explaining the relationship between fineness, C_3S and strength. The equation which defines this relationship is :

$$\textbf{Strength} = -7.80 + 0.267(C_3S) + 0.274(\textbf{Fineness})$$

With the elimination of C_2S, C_3A and C_4AF from the model but with the accuracy remaining the same, it can be confidently said that the model in case 3 is mathematically the most "economical" linear model for compressive strength and the effects of the measured variables.

9.6 LIMITATIONS OF THE MODEL

Although the present model relates the chemical composition and fineness to strength, there are a number of limitations that should be borne in mind :

(a) The model is only capable of predicting for 28 day strengths, and if the analysis is to be used for early or later ages, the coefficients will have to be re-established.

(b) For later ages, allowance must be made for the contribution that C_2S makes to strength.

(c) There is a need to consider the influence of C_3A on strength. From this research it does not appear that the model would be greatly improved by taking this compound into account and although there are considerable differences of opinion on the relevance of C_3A, some research studies have shown that the strength developed by C_3S depends on the proportion of C_3A in the cement[9.2].

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CHAPTER 10

CONCLUSIONS

The results of tests conducted in this research indicate that the chemical composition and fineness of Ordinary Portland cement have a significant influence on the compressive strength of cement mortar. In drawing conclusions from this research, it must be noted that the results are based on a fairly limited amount of test data and that the variations in some of the chemical compositions are not significant.

1. Bleeding : The bleeding process common in cement mortar and concrete can be prevented (for laboratory testing) by rotating the specimen.

2. Air entrapment : The evacuation of cement paste eliminated vast amounts of entrapped air but this test cannot be applied to cement mortar or concrete as it tends to cause the mix constituents to segregate.

3. X-ray diffraction : The results indicated that XRD is a reliable method capable of reproducible results.

   The straight line method of integrating the area under an X-ray diffraction peak generally shows less variation than the polynomial method.

   The sample thickness and grain size of the cement sample can influence the predetermined position of the X-ray peaks.

   Preferential alignment can cause slight fluctuations in the X-ray peak height and areas.

4. Cement compounds : The single regression analysis performed on the chemical compounds showed that dicalcium silicate does not affect the compressive strength at 28 days and that, although tetracalcium aluminoferrite's influence is minimal, it appears to have a negative influence on the compressive strength.

   Tricalcium silicate has a positive influence on the compressive strength and its rate of hydration does not appear to be influenced by the tricalcium aluminate content.

5. Fineness of cement : The "coarse" particles (>47.3μm) exert a little influence on the 28 day compressive strength.

The "medium" sized particles, within the size range 8.48μm to 47.3μm have a strong positive influence on the compressive strength. This is therefore the major particle size range necessary to be considered.

6. The combined effect of fineness and cement compounds: As the chemical compounds and the fineness all interact, their influences on the compressive strength had to be compared in a multiple regression analysis.

The cement compounds C_3A, C_2S and C_4AF have an insignificant effect on the 28 day compressive strength of cement.

The cement compound C_3S and the percentage particles between the size range 8.48μm and 47.3μm have a major effect on the 28 day compressive strength.

7. Strength prediction model : The model derived represents the compressive strength (in MPa) of 100mm mortar cubes at age 28 days. The best formula determined in this investigation is represented by :

Strength = -7.800 + 0.267(C_3S) + 0.274(Fineness)

The model is not suitable for either early age or later age testing as the chemical compounds and the size range of the particles which affect the compressive strength will have different contributions to the strength.

CHAPTER 11

RECOMMENDATIONS

Based on the findings and conclusions of this research, the following recommendations can be made :

1. The accuracy of the X-ray diffraction results can be improved by preventing the crystals in the cement from becoming preferentially aligned, by controlling the thickness of the sample and by grinding the cement to greater finenesses.

2. The model can be adapted to enable strength predictions to be made for ages other than 28 days.

3. Cement samples with larger variations in the chemical composition should be tested to improve the reliability of the proposed model.

4. Tricalcium aluminate should be given special attention in further research to determine its effect on strength.

CHAPTER 12

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APPENDICES

APPENDIX 1

COMPARATIVE TESTING

Ready Mix Materials

(Pty) Limited (Reg No. 87/00894/07)

3rd Floor Taeuber & Corssen Building 16 Milner Street Metro Industria		3de Verdieping Taeuber & Corssen Gebou Milnerstraat 16 Metro Industria
P.O. Box	139	Posbus
Paarden Eiland	7420	Paarden Eiland
South Africa		Suid Afrika
Telephone	(021) 511-0002	Telefoon
Telex	5-26455	Teleks
Telefax	(021) 511-9530	Telefaks

REPORT ON COMPRESSIVE STRENGTH OF CONCRETE SPECIMENS
(TEST METHOD S.A.B.S. 863)

Dear Sirs,

The following cube results relate to interlaboratory tests performed between the four laboratories mentioned below. All cubes were made from a single batch of concrete.

NO.	RMM	SABS	PCI	UCT	COMMENTS
A	44,5	46,0	42,5	44,5	
B	44,5	48,0	43,0	46.0	
C	39,5	50,0	43,5	46.5	
AVE	43,0	48,0	43,0	45.5	

CASTING DATE : 15.07.91

DATE TESTED : 22.07.91

CUBE REF. : 4850

Yours faithfully,
READY MIX MATERIALS

L. HENDRICKS
LABORATORY SUPERVISOR

A. VENIER
TECHNICAL CONTROLLER

APPENDIX 3

PHILIPS DIFFRACTOMETER

APPENDIX 4

GYPSUM : INTERPLANAR SPACINGS AND CORRESPONDING ANGLES

Interplanar spacings, percentage "visibility" in comparison to the largest peak and the diffraction angle for the three common forms of gypsum. This table is a record of the three gypsum diffractometer patterns. It was used to identify the gypsum in the cement and to check that it did not interfere with the relevant chemical compound peaks.

CALCIUM SULPHATE		
DI HYDRATE	ANHYDRITE	HYDRATE
$CaSO_4.2H_2O$	$CaSO_4$	$CaSO_4.H_2O$

d (Å)	%	BRAGG ANGLE	d (Å)	%	BRAGG ANGLE	d (Å)	%	BRAGG ANGLE
7.6	100	11.71	3.87	6	22.98	6.01	95	14.74
4.27	50	20.80	3.49	100	25.52	4.35	2	20.42
3.79	20	23.47	3.11	4	28.70	3.46	45	25.75
3.163	4	28.21	2.849	35	31.40	3.21	2	27.79
3.059	55	29.19	2.79	4	32.08	3.3	6	27.02
2.867	25	31.20	2.473	8	36.33	3.001	100	29.77
2.786	6	32.13	2.328	20	38.68	2.8	50	31.96
2.769	28	32.33	2.208	20	40.87	2.712	4	33.03
2.591	4	34.62	2.183	8	41.36	2.704	2	33.13
2.53	1	35.48	2.086	10	43.38	2.342	2	38.44
2.495	6	36.00	1.993	6	45.51	2.336	2	38.54
2.45	4	36.68	1.938	4	46.88	2.27	4	39.71
2.4	4	37.47	1.869	16	48.72	2.183	2	41.36
2.216	6	40.72	1.852	4	49.20	2.135	10	42.33
2.139	2	42.25	1.749	12	52.31	1.132	6	85.84
2.08	10	43.51	1.748	10	52.34	2.111	2	42.84
2.073	8	43.66	1.648	14	55.78	2	2	45.34
1.99	4	45.58	1.594	4	57.84	1.908	4	47.66
1.953	2	46.50	1.564	6	59.06	1.842	12	49.48

d (Å)	%	BRAGG ANGLE	d (Å)	%	BRAGG ANGLE	d (Å)	%	BRAGG ANGLE
1.898	16	47.93	1.525	4	60.73	1.839	6	49.57
1.879	10	48.44	1.515	2	61.17	1.735	4	52.76
1.864	4	48.86	1.49	6	62.31	1.732	4	52.86
1.843	2	49.45	1.424	4	65.55	1.693	8	54.17
1.812	10	50.36	1.418	2	65.87	1.665	8	55.16
1.796	4	50.84	1.398	4	66.93	1.501	2	61.81
1.778	10	51.39	1.396	2	67.04			
1.711	2	53.56	1.365	2	68.77			
1.684	2	54.49	1.319	4	71.53			
1.664	4	55.20	1.296	2	73.00			
1.645	2	55.89	1.277	6	74.27			
1.621	6	56.79	1.237	2	77.10			
1.599	1	57.65	1.216	4	78.69			
1.584	2	58.25	1.199	2	80.02			
1.532	2	60.42	1.178	1	81.75			
1.522	2	60.86	1.166	4	82.78			

Note : The letter "d" represents the inter lattice spacing in Angstrom's (Å) and the letter "%" represents the size of the peak in comparison to the largest peak which is presented as 100%.

APPENDIX 5

VALUES OF CORRELATION COEFFICIENT

Degrees of Freedom	1 variable	2 variables	3 variables	4 variables
1	.997	.999	.999	.999
2	.950	.975	.983	.987
3	.878	.930	.950	.961
4	.811	.881	.912	.930
5	.754	.836	.874	.898
6	.707	.795	.839	.867
7	.666	.758	.807	.838
8	.632	.726	.777	.811
9	.602	.697	.750	.786
10	.576	.671	.726	.763
11	.553	.648	.703	.741
12	.532	.627	.683	.722
13	.514	.608	.664	.703
14	.497	.590	.646	.686
15	.482	.574	.630	.670
16	.468	.559	.615	.655
17	.456	.545	.601	.641
18	.444	.532	.587	.628
19	.433	.520	.575	.615

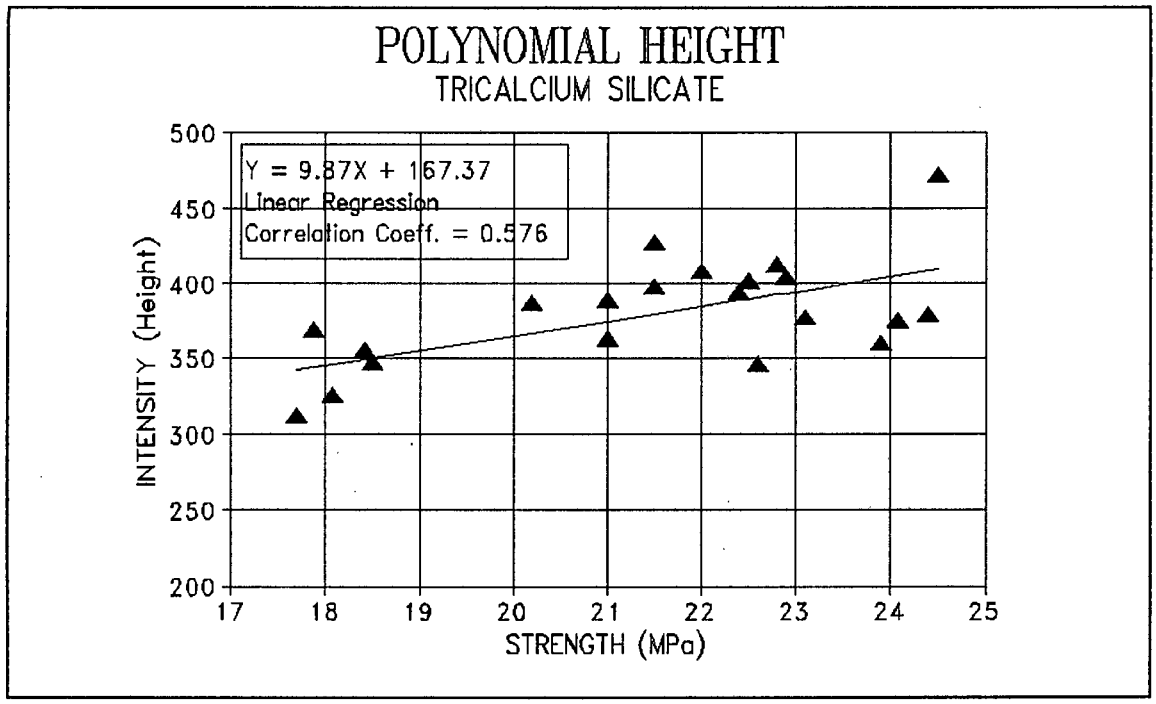
Degrees of Freedom	1 variable	2 variables	3 variables	4 variables
20	.423	.509	.563	.604
21	.413	.498	.552	.592
22	.404	.488	.542	.582
23	.396	.479	.532	.572
24	.388	.470	.523	.562
25	.381	.462	.514	.553
26	.374	.454	.506	.545
27	.367	.446	.498	.536
28	.361	.439	.490	.529
29	.355	.432	.482	.521
30	.349	.426	.476	.514
35	.325	.379	.445	.482
40	.304	.373	.419	.455
45	.288	.353	.397	.432
50	.273	.336	.379	.412

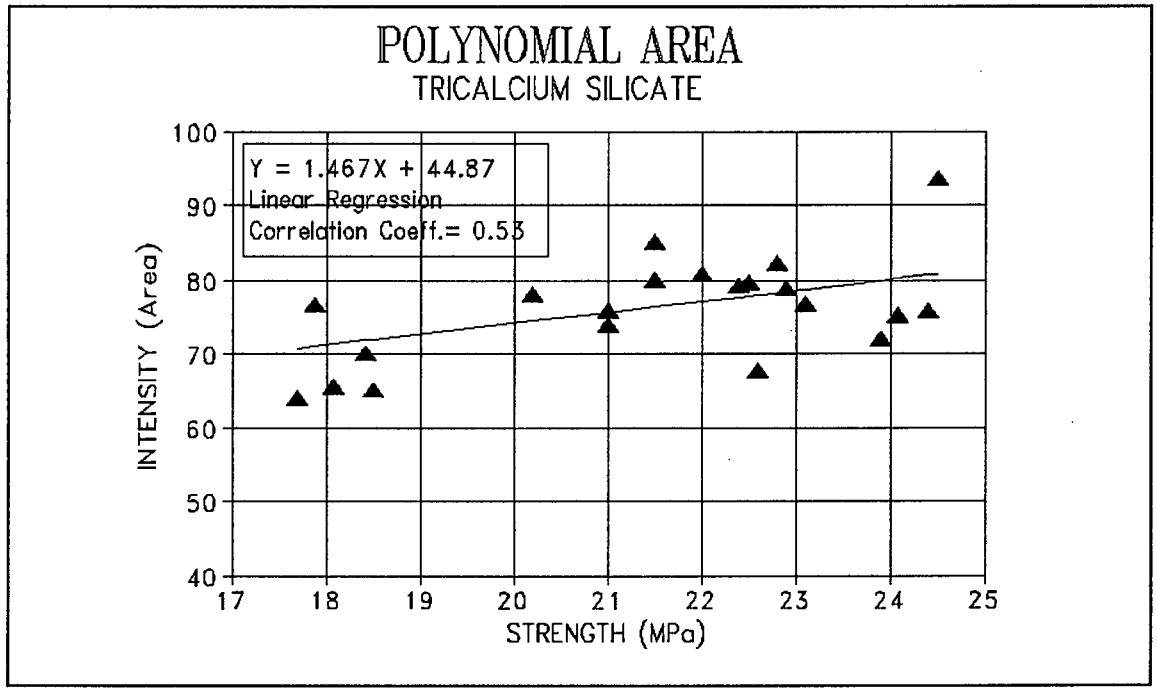
If the computed value of the correlation coefficient (r) is greater than the value in the above table, at the given level and for a certain degree of freedom, then the correlation between the variable(s) is said to be significant. This table has been reproduced from : Basic Statistical Methods for Engineers and Scientists, Third edition.

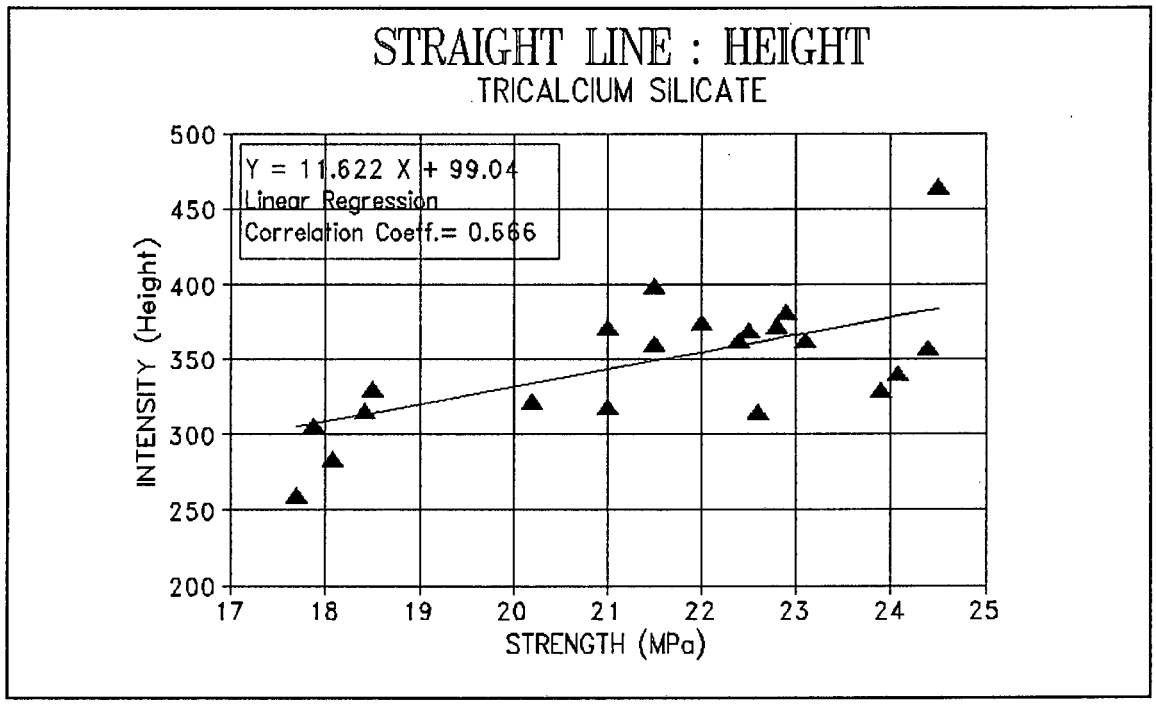
APPENDIX 6

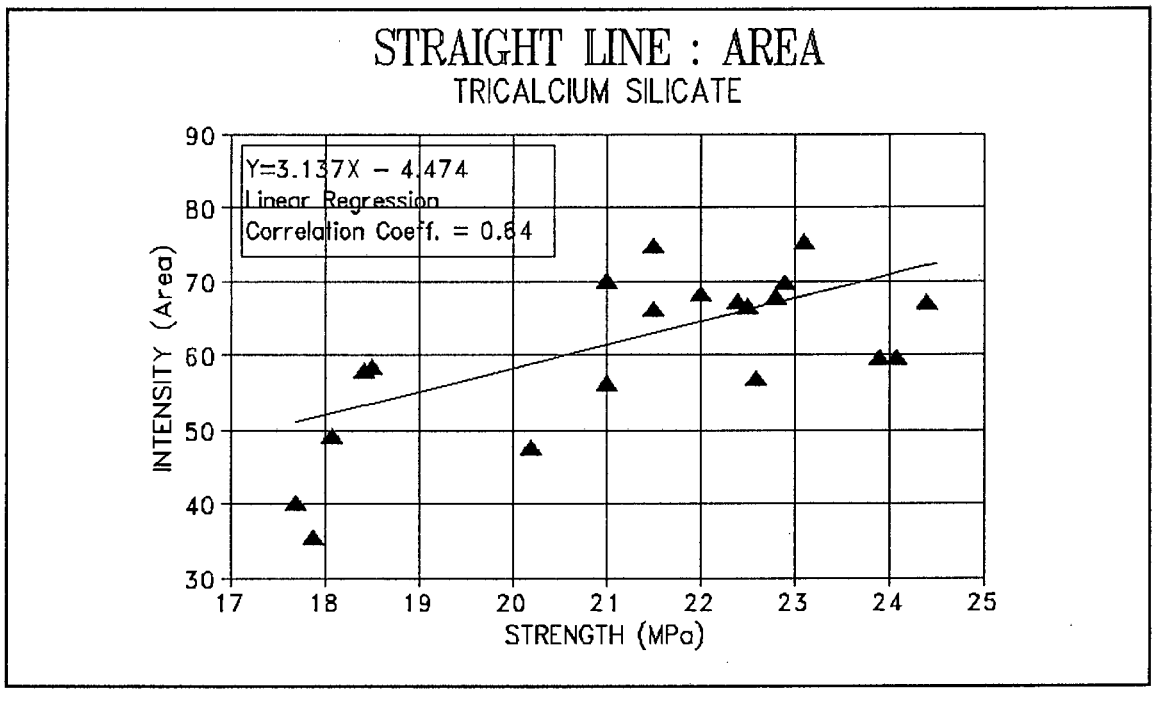
REGRESSION ANALYSIS OF THE EFFECT OF THE MAJOR CHEMICAL COMPOUNDS ON COMPRESSIVE STRENGTH

TRICALCIUM SILICATE (C_3S)

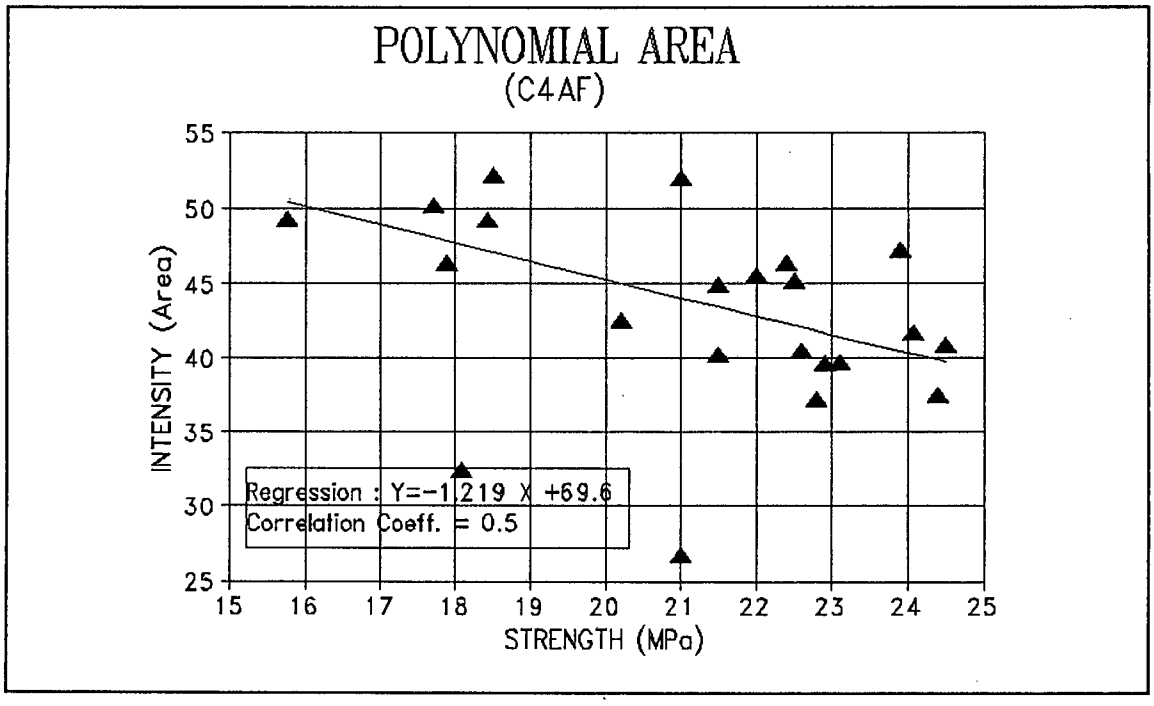


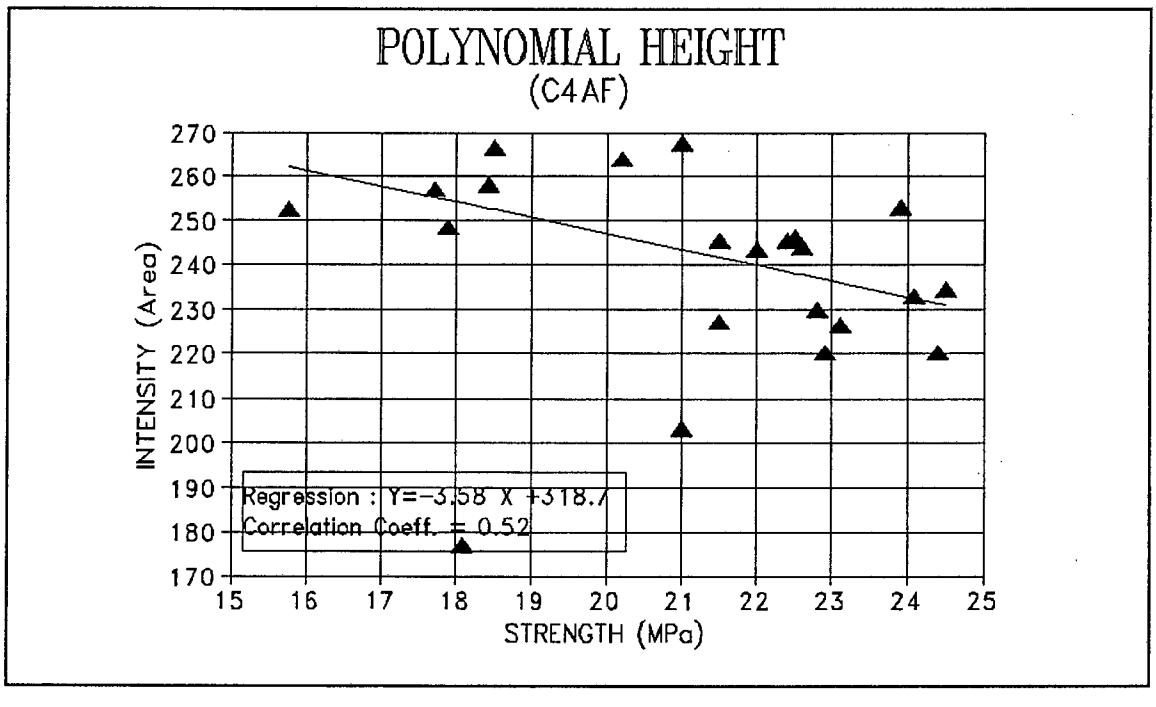


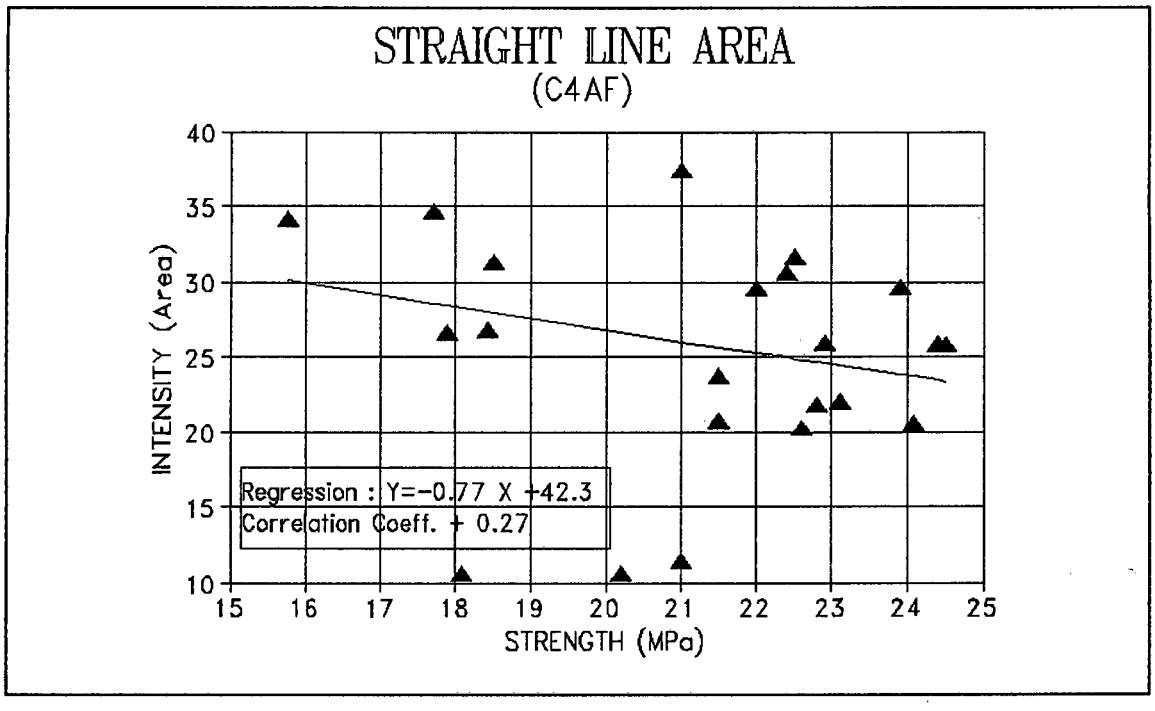

STRAIGHT LINE : HEIGHT
TRICALCIUM SILICATE
Y = 11.622 X + 99.04
Linear Regression
Correlation Coeff.= 0.666
INTENSITY (Height)
STRENGTH (MPa)
500
450
400
350
300
250
200
17
18
19
20
21
22
23
24
25

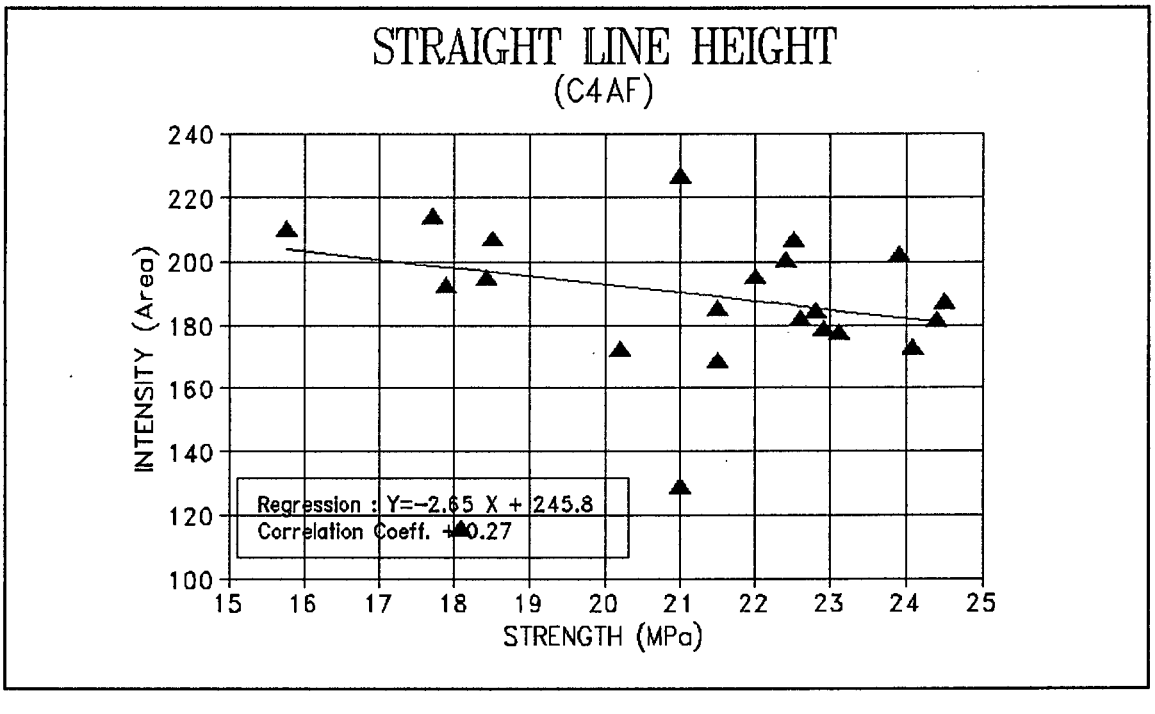

STRAIGHT LINE : AREA
TRICALCIUM SILICATE
Y=3.137X - 4.474
Linear Regression
Correlation Coeff. = 0.84
INTENSITY (Area)
STRENGTH (MPa)
90
80
70
60
50
40
30
17
18
19
20
21
22
23
24
25

TETRACALCIUM ALUMINOFERRITE (C_4AF)

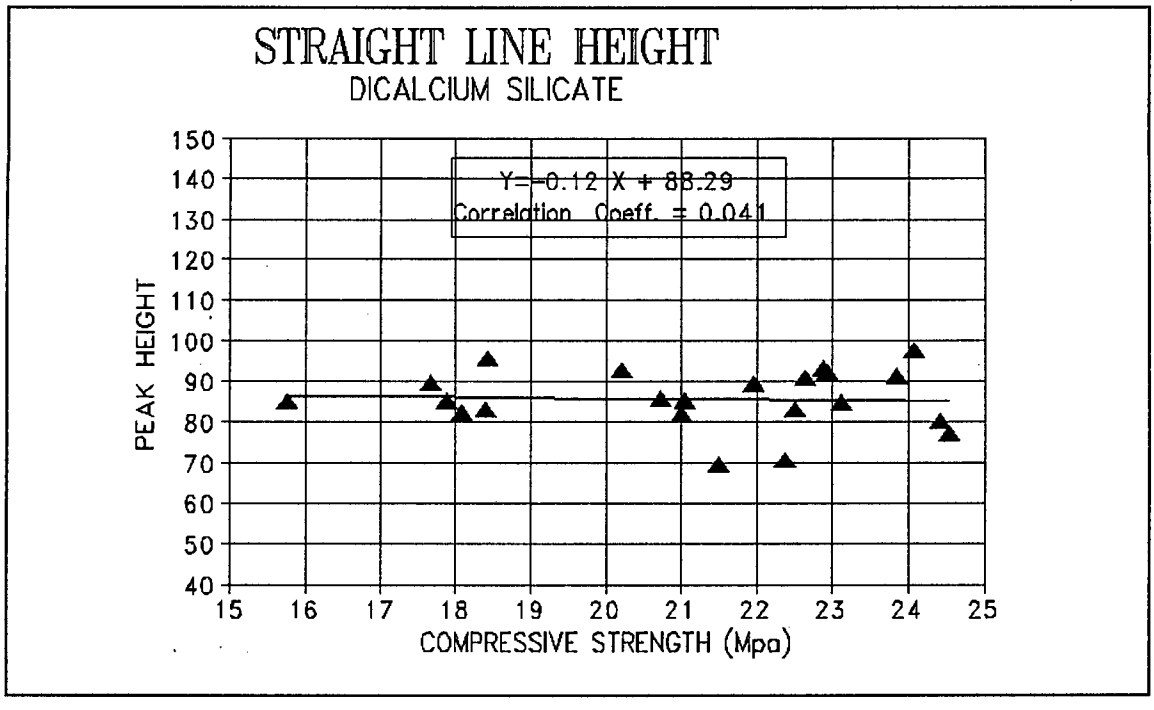


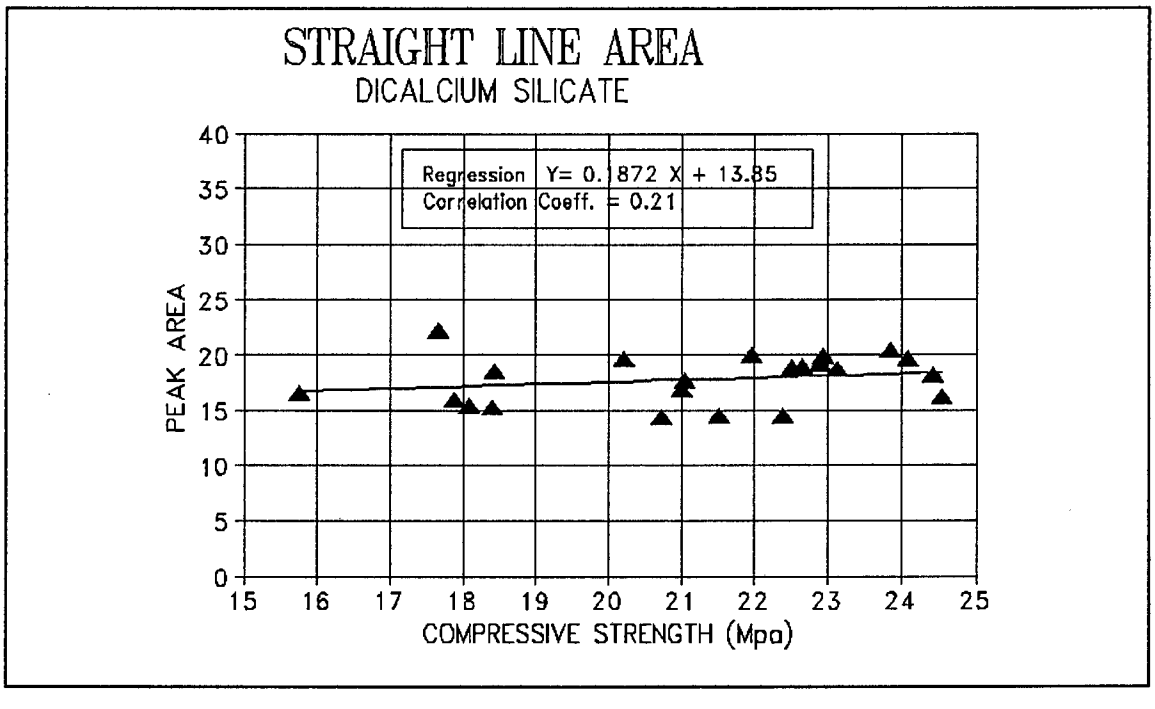


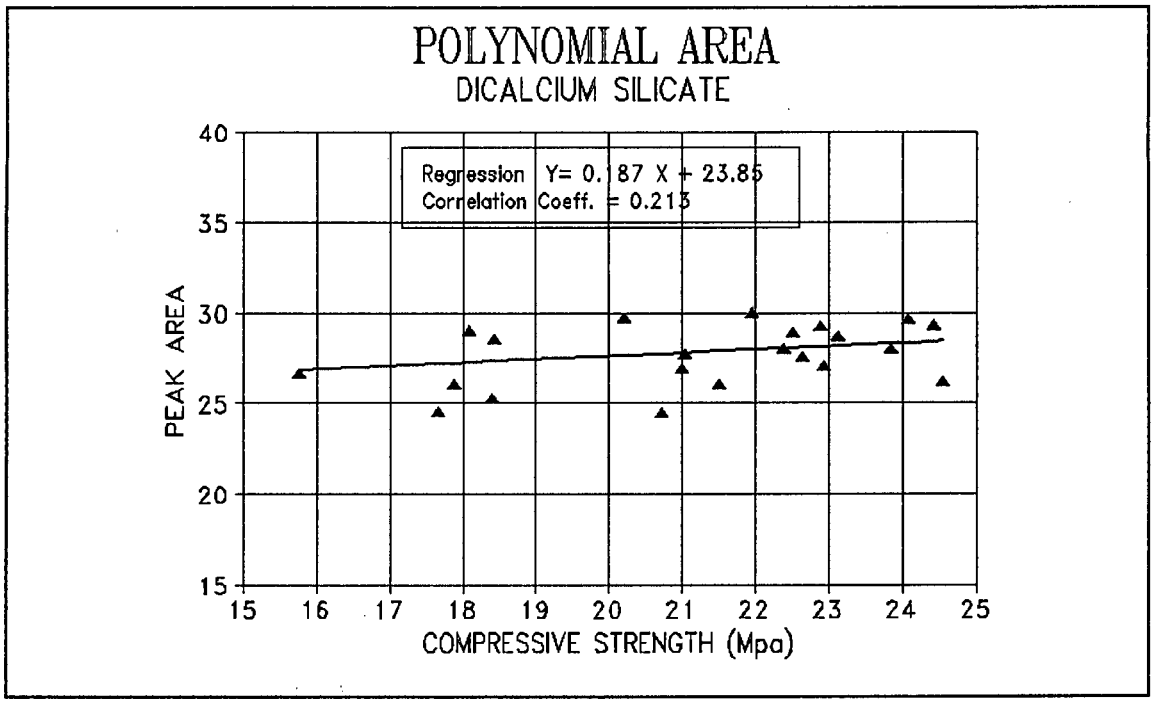

STRAIGHT LINE AREA
(C4AF)
INTENSITY (Area)
STRENGTH (MPa)
Regression : Y=-0.77 X +42.3
Correlation Coeff. = 0.27
40
35
30
25
20
15
10
15
16
17
18
19
20
21
22
23
24
25

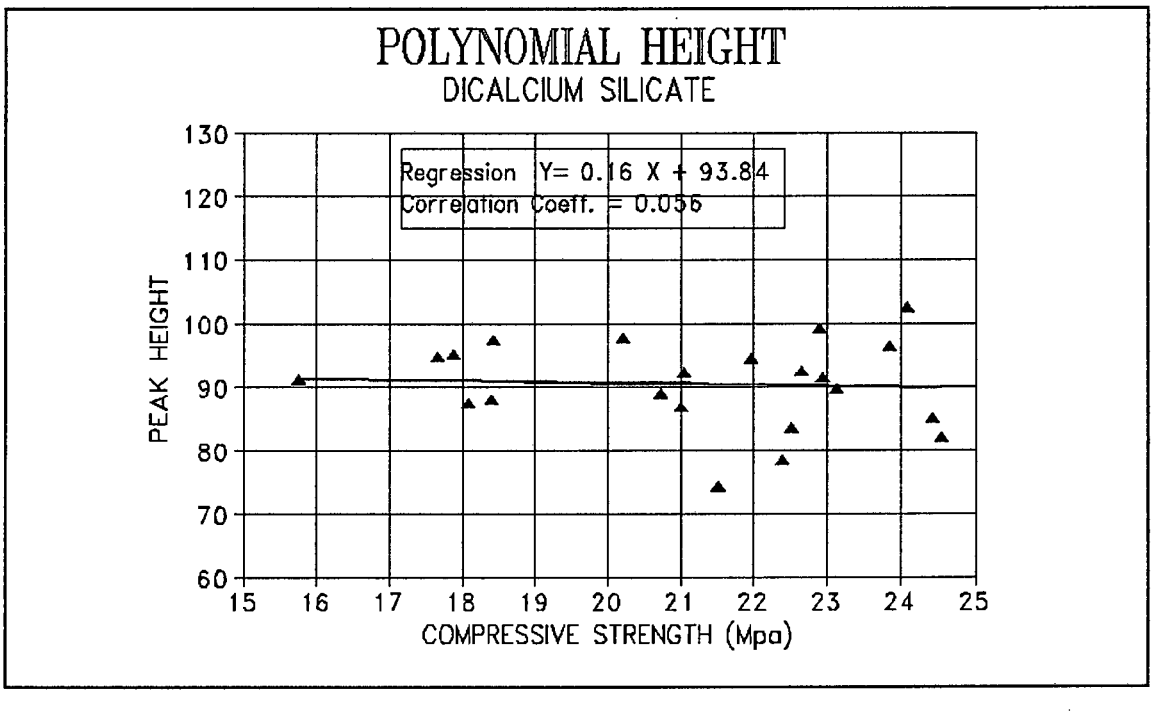

STRAIGHT LINE HEIGHT
(C4AF)
INTENSITY (Area)
STRENGTH (MPa)
Regression : Y=-2.65 X + 245.8
Correlation Coeff. = 0.27
240
220
200
180
160
140
120
100
15
16
17
18
19
20
21
22
23
24
25

DICALCIUM SILICATE (C_2S)

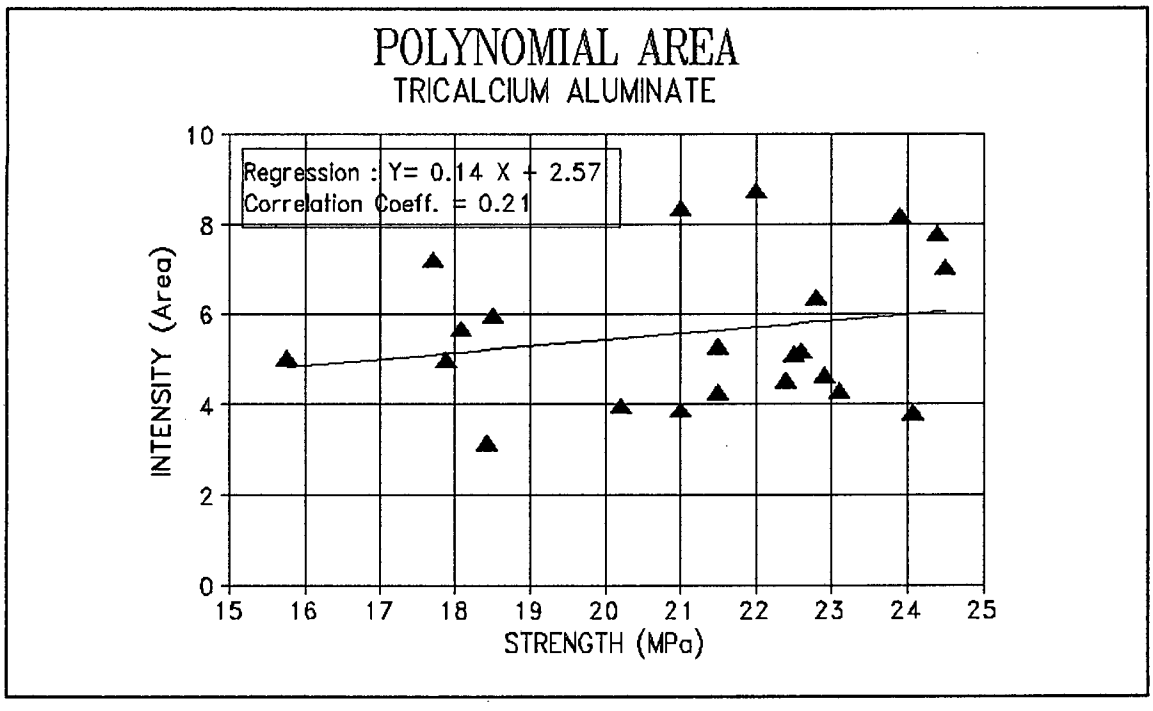


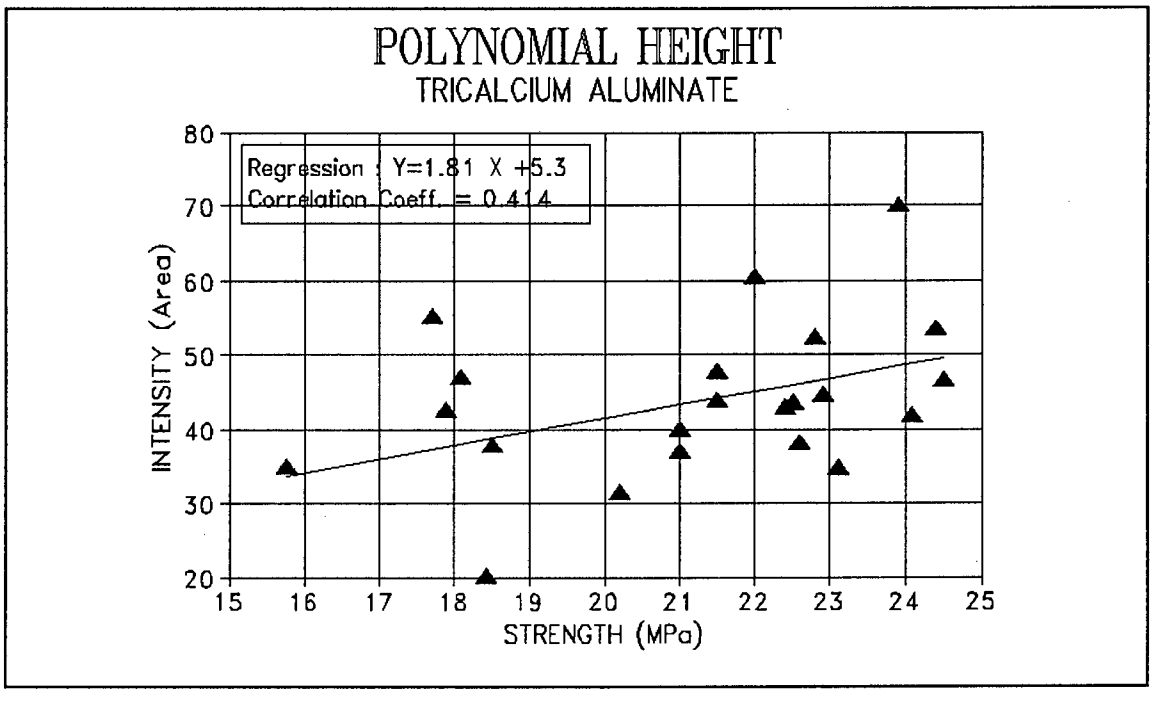


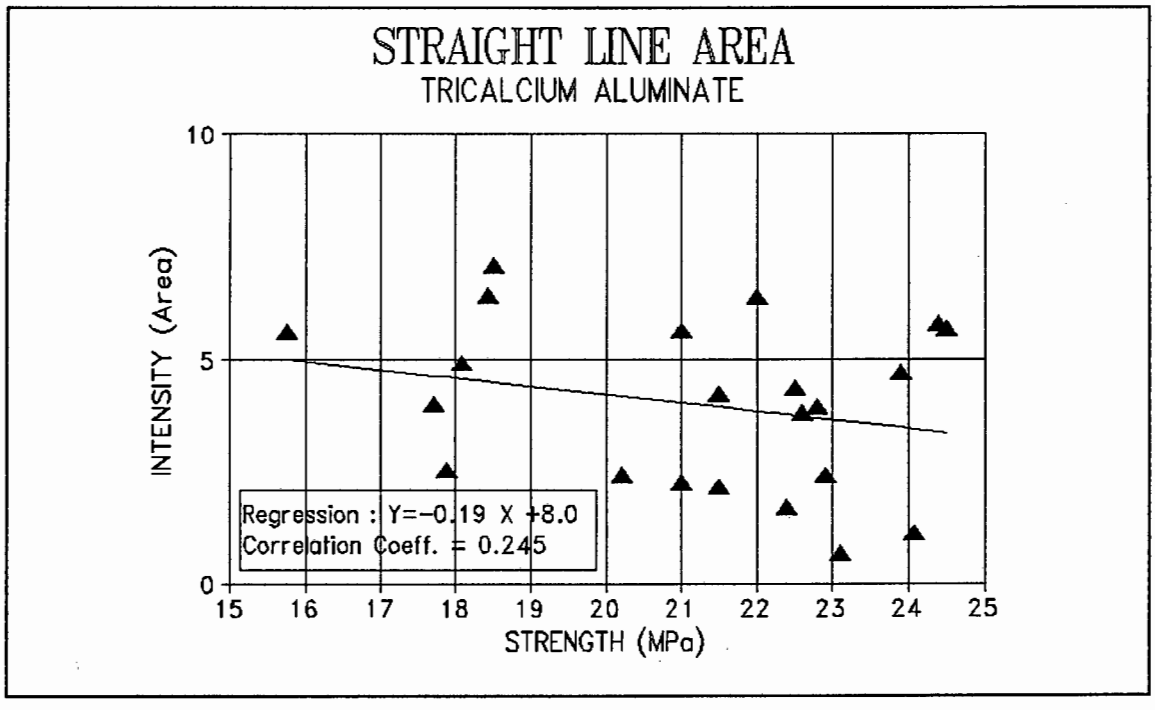

POLYNOMIAL AREA
DICALCIUM SILICATE
Regression Y= 0.187 X + 23.85
Correlation Coeff. = 0.213
PEAK AREA
40
35
30
25
20
15
15 16 17 18 19 20 21 22 23 24 25
COMPRESSIVE STRENGTH (Mpa)


POLYNOMIAL HEIGHT
DICALCIUM SILICATE
Regression Y= 0.16 X + 93.84
Correlation Coeff. = 0.056
PEAK HEIGHT
130
120
110
100
90
80
70
60
15 16 17 18 19 20 21 22 23 24 25
COMPRESSIVE STRENGTH (Mpa)

TRICALCIUM ALUMINATE (C_3A)






STRAIGHT LINE AREA
TRICALCIUM ALUMINATE
INTENSITY (Area)
STRENGTH (MPa)
Regression : Y=-0.19 X +8.0
Correlation Coeff. = 0.245
0
5
10
15
16
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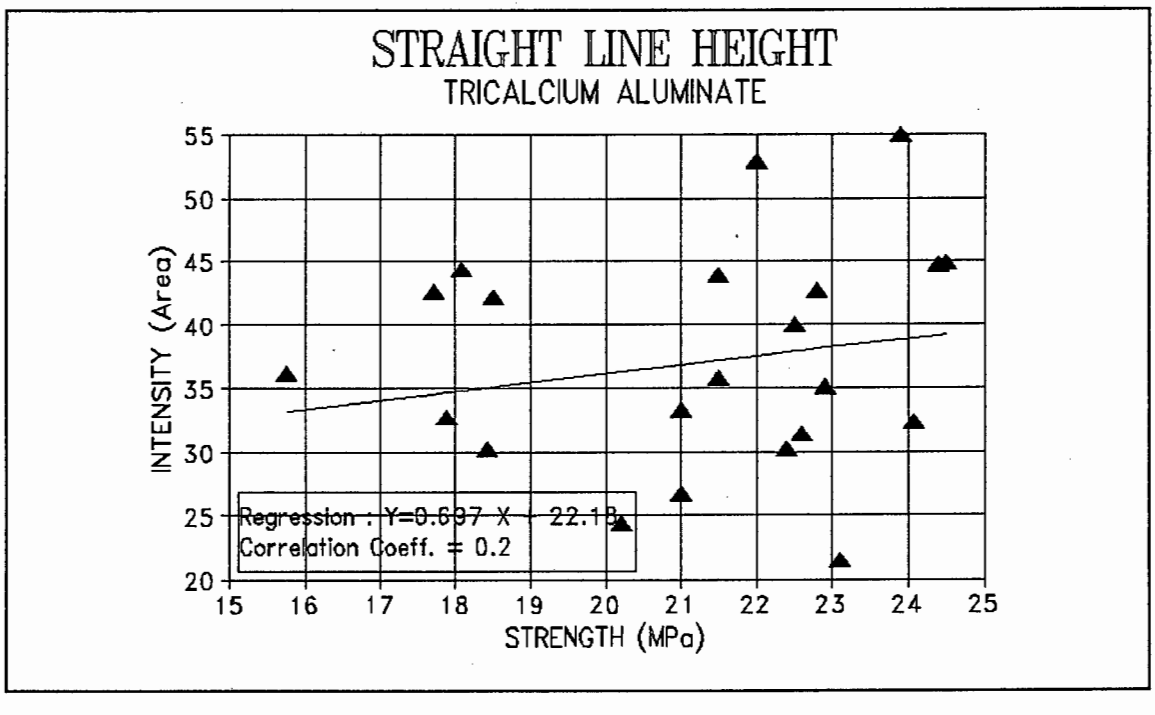
STRAIGHT LINE HEIGHT
TRICALCIUM ALUMINATE
INTENSITY (Area)
STRENGTH (MPa)
Regression : Y=0.697 X + 22.13
Correlation Coeff. = 0.2
20
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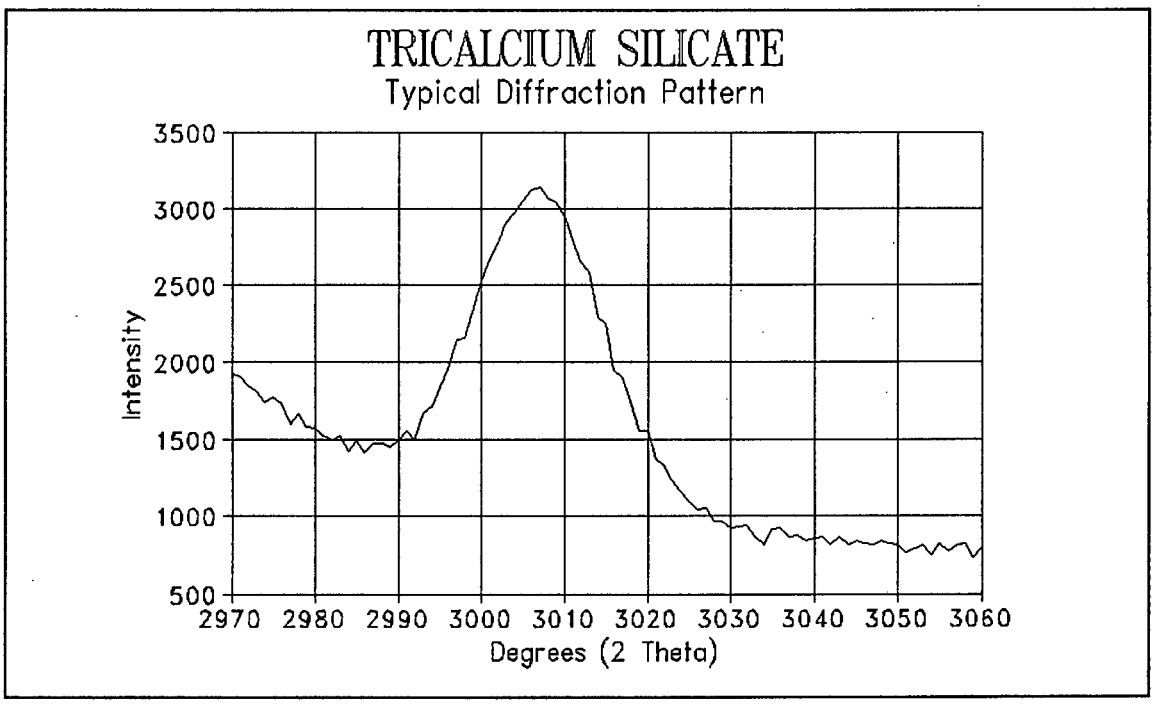
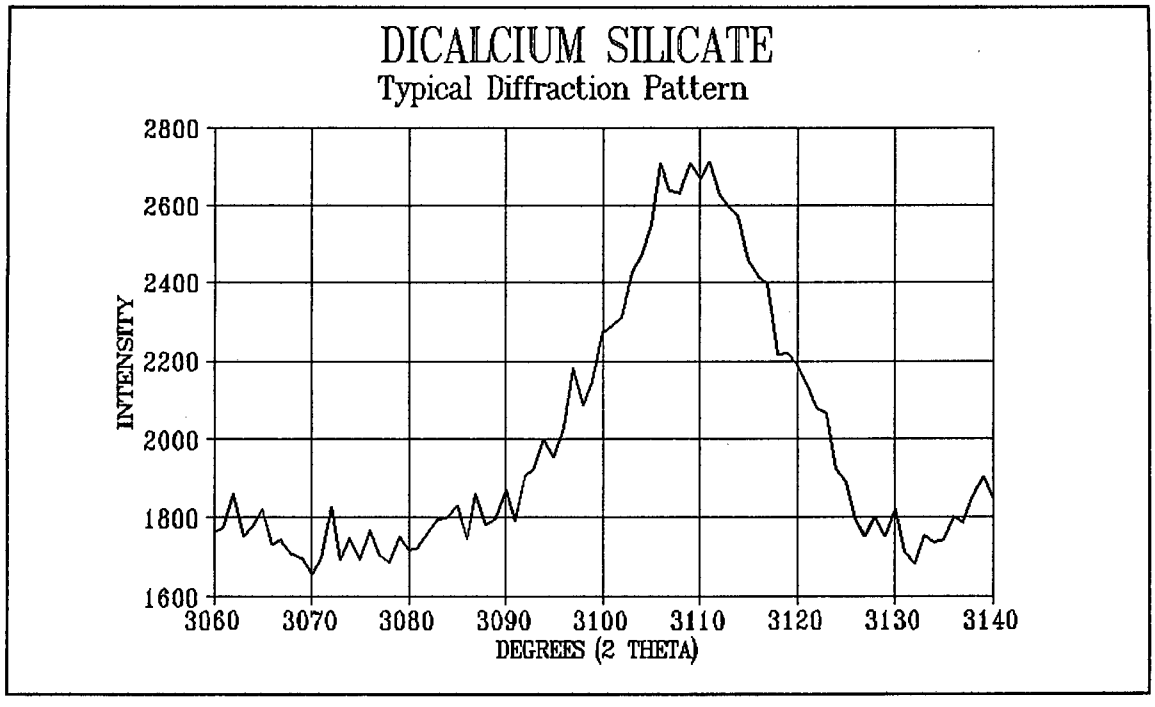
APPENDIX 7

TYPICAL COMPOUND DIFFRACTION PATTERNS

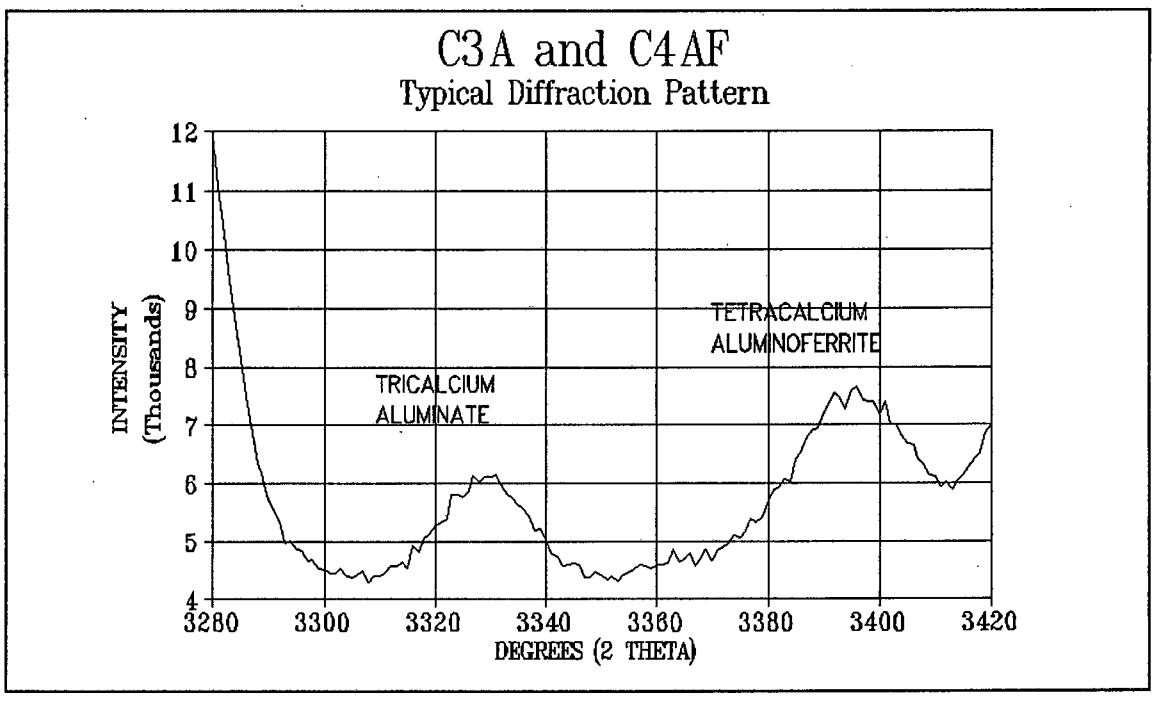
TRICALCIUM SILICATE



DICALCIUM SILICATE



TETRACALCIUM ALUMINOFERRITE AND TRICALCIUM ALUMINATE



APPENDIX 8

THE VALUES OF VARIABLES USED FOR THE MULTIPLE REGRESSION ANALYSIS

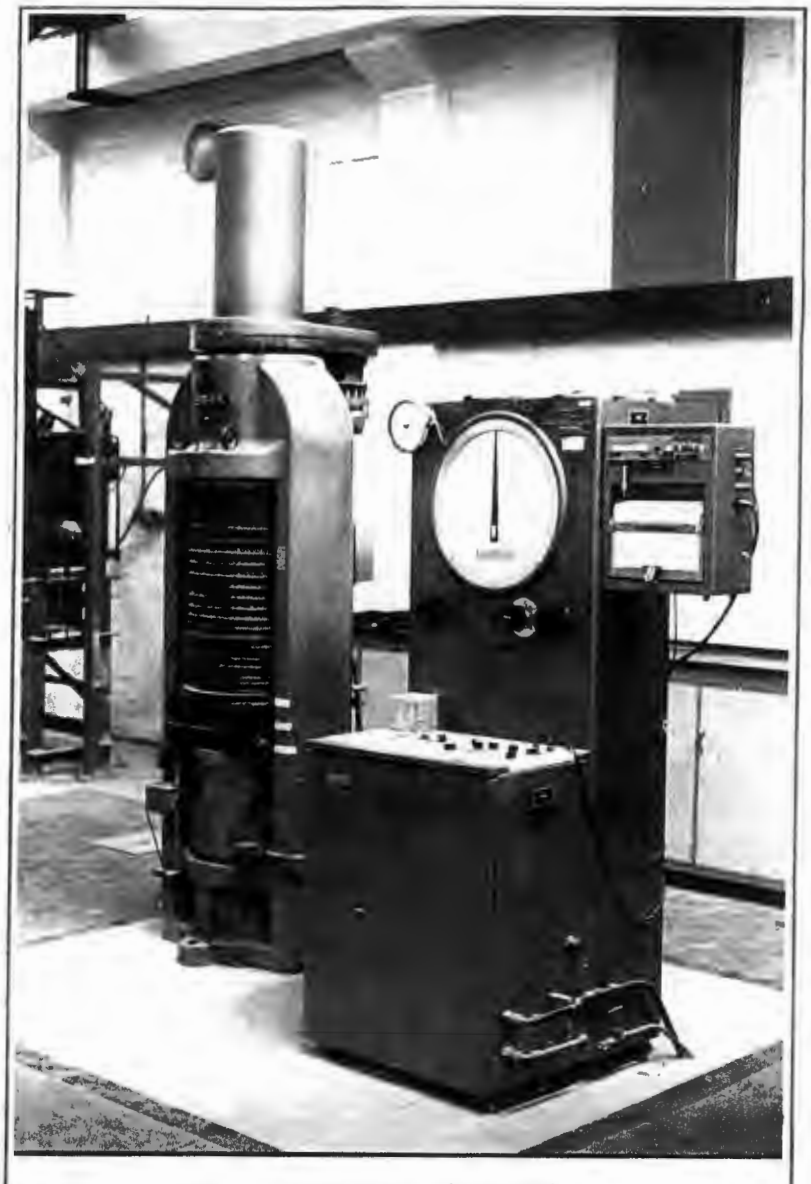
C_2S (%)	C_3A (%)	C_3S (%)	C_4AF (%)	FINENESS	STRENGTH (MPa)
34.4	2.9	49.1	11.7	46.7	15.7
38.5	3.6	34.4	12.7	52.7	17.6
35.4	2.7	49.4	11.0	49.4	17.8
37.8	4.0	50.6	7.34	52.61	18.0
37.6	2.4	48.3	10.6	47.6	18.4
32.8	3.3	50.7	11.3	48.9	18.4
37.4	1.9	50.5	9.59	52.9	20.2
31.5	1.9	53.1	11.5	53.6	20.7
36.4	2.8	52.9	7.62	63.29	21.0
29.9	2.6	56.7	9.34	48.5	21.0
28.1	3.5	57.0	9.47	58.63	21.5
32.3	3.8	52.6	9.74	56.28	21.9
28.1	2.4	56.2	11.0	55.1	22.3
31.0	3.0	53.6	10.6	63.18	22.5
36.7	2.5	49.5	10.2	54.8	22.6
33.9	3.1	52.6	9.28	60.31	22.8
33.5	2.5	54.0	8.98	61.27	22.9
32.9	1.6	54.8	9.55	56.8	23.1

C_2S (%)	C_3A (%)	C_3S (%)	C_4AF (%)	FINENESS	STRENGTH (MPa)
34.8	4.2	48.7	10.6	60.07	23.8
37.3	2.4	50.5	9.14	55.9	24.0
31.1	3.5	54.0	9.76	53.1	24.4
25.8	3.0	60.7	8.70	57.04	24.5

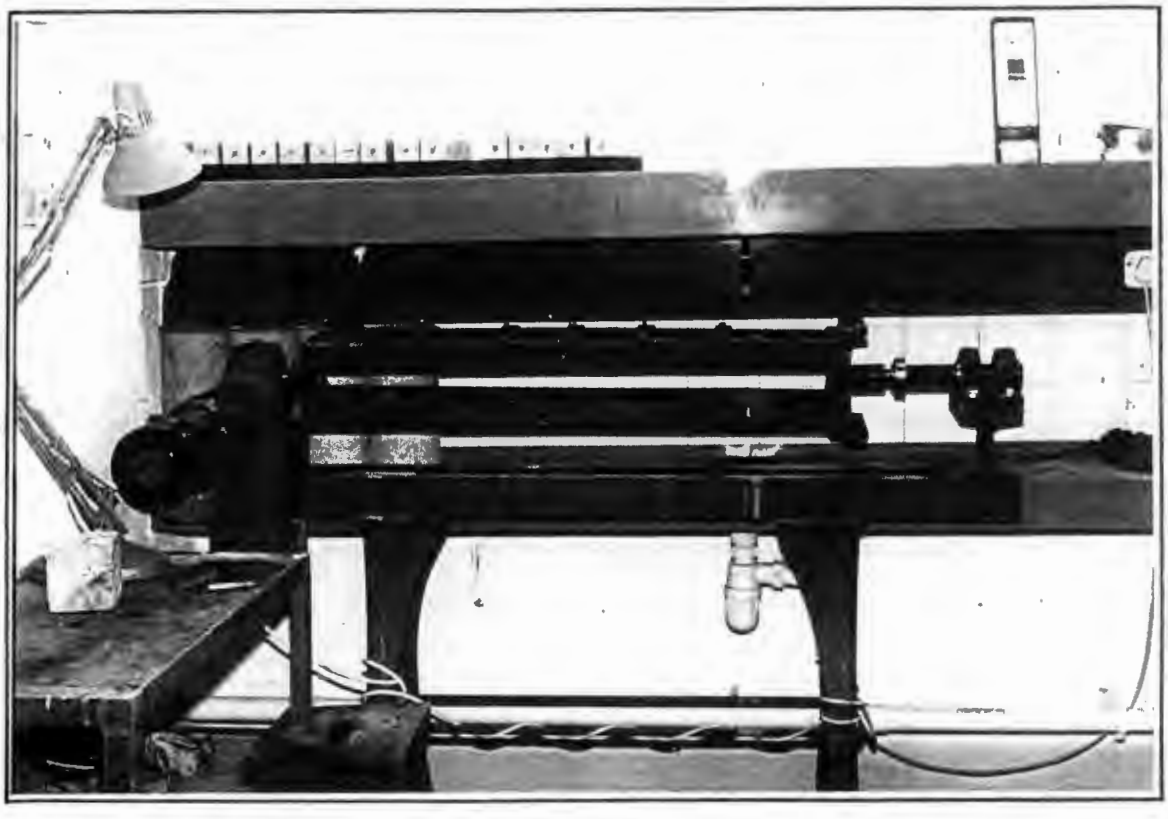
* **Note :** "Fineness" represents the percentage of the cement particles within the size band 47.3 microns to 8.48 microns.

APPENDIX 9

PHOTOGRAPHS



The Amsler compressive machine



The "bleeding" rotation apparatus

A typical cube mould

APPENDIX 10

FINENESS ANALYSIS

(example of the fineness data used in this research)

Sample	% in size band 180-57.3	% in size band 57.3-47.3	% in size band 47.3-18.2	% in size band 18.2-8.48	% in size band 8.48-0	Total %
K	24.1	8.0	35.5	15.0	17.4	100
N	27.7	8.2	33.9	14	16.2	100
O	27.3	8.0	33.6	14	17.1	100
Z	34.6	7.6	29.4	11.8	16.6	100
BB	34.2	7.5	30.0	12.3	16.0	100
AA	36.4	7.4	28.6	12.1	15.5	100
V	27.9	8.1	33.2	14.4	16.4	100
Y	32.0	8.0	31.1	12.9	16.0	100
Q	26.6	8.3	34.9	14.4	15.8	100
G	28.5	8.0	35.1	14.1	14.3	100
T	32.9	7.5	30.1	13.0	16.5	100
L	24.4	8.3	36.3	14.7	16.3	100

FINENESS ANALYSIS DATA

(Typical Malvern Laser results)

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:16 pm

UCT K 16-3

DISPERSANT : WATER
STIRRER : 80 %
PUMP : 80 %
ULTRASONIC : 50 %
ANALYST :

3793 stnd 1HU427M **ALARMS SET A B C **

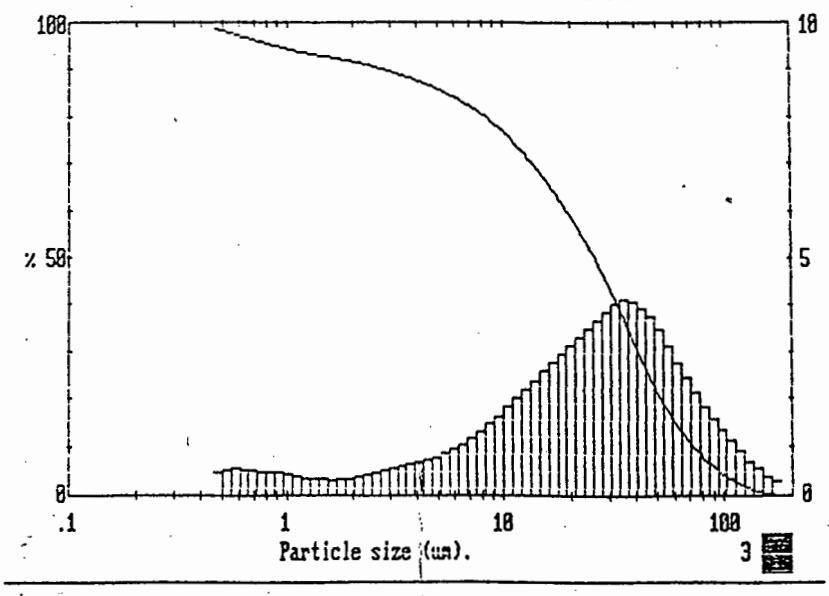
Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.77
				39.1	8.4	32.3	59.5	3.95	1.3	3.27	10.6	
				32.3	7.9	26.7	51.6	3.27	1.1	2.70	9.5	D[4,3] 33.48µm
				26.7	7.2	22.0	44.4	2.70	1.0	2.23	8.6	
				22.0	6.4	18.2	38.0	2.23	0.8	1.84	7.8	
180	0.7	149	99.3	18.2	5.7	15.1	32.4	1.84	0.7	1.52	7.1	D[3,2] 5.47µm
149	1.3	123	97.9	15.1	4.9	12.4	27.5	1.52	0.7	1.26	6.4	
123	2.1	102	95.8	12.4	4.1	10.3	23.4	1.26	0.8	1.04	5.6	
102	3.1	83.9	92.7	10.3	3.3	8.48	20.0	1.04	0.9	0.86	4.7	D[v,0.9] 73.92µm
83.9	4.2	69.3	88.4	8.48	2.6	7.01	17.4	0.86	1.0	0.71	3.7	
69.3	5.6	57.3	82.9	7.01	2.1	5.79	15.2	0.71	1.0	0.59	2.6	
57.3	7.0	47.3	75.9	5.79	1.8	4.79	13.5	0.59	1.2	0.48	1.4	D[v,0.1] 2.94µm
47.3	8.0	39.1	67.9	4.79	1.5	3.95	12.0	0.48	1.4	0.20	0.0	

Source = :Sample
Focal length = 100 mm
Presentation = stnd.

Beam length = 2.2 mm
Residual = 0.223 %
Obscuration = 0.2288
Volume distribution

Model indp
Volume Conc. = 0.0285%
Sp.S.A 1.0960 m²/cc.

D[v,0.5] 25.62µm



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:19 pm

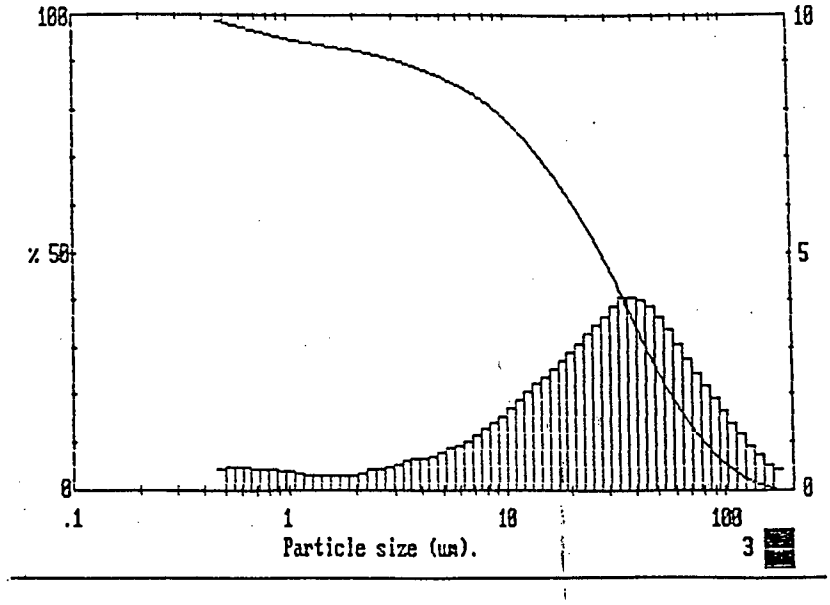
UCT N 19-3

DISPERSANT : WATER
STIRRER : 80 %
PUMP : 80 %
ULTRASONIC : 50 %
ANALYST :

3793 stnd 1KU427M **ALARMS SET A B C **

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.78
				39.1	8.3	32.3	55.8	3.95	1.3	3.27	9.6	
				32.3	7.6	26.7	48.3	3.27	1.1	2.70	8.6	D[4,3] 36.39µm
				26.7	6.8	22.0	41.5	2.70	0.9	2.23	7.7	
				22.0	6.0	18.2	35.5	2.23	0.7	1.84	7.0	
180	1.0	149	99.0	18.2	5.3	15.1	30.2	1.84	0.6	1.52	6.3	D[3,2] 5.97µm
149	1.7	123	97.2	15.1	4.6	12.4	25.7	1.52	0.6	1.26	5.7	
123	2.7	102	94.5	12.4	3.8	10.3	21.9	1.26	0.7	1.04	5.0	
102	3.8	83.9	90.8	10.3	3.2	8.48	18.7	1.04	0.8	0.86	4.2	D[v,0.9] 81.16µm
83.9	4.9	69.3	85.9	8.48	2.5	7.01	16.2	0.86	0.9	0.71	3.3	
69.3	6.2	57.3	79.7	7.01	2.0	5.79	14.1	0.71	0.9	0.59	2.3	
57.3	7.4	47.3	72.3	5.79	1.7	4.79	12.4	0.59	1.1	0.48	1.3	D[v,0.1] 3.46µm
47.3	8.2	39.1	64.1	4.79	1.5	3.95	10.9	0.48	1.3	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 27.93µm
	Residual = 0.217 %		
Focal length = 100 mm	Obscuration = 0.1208	Volume Conc. = 0.0153%	
Presentation = stnd·	Volume distribution	Sp.S.A 1.0053 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:22 pm

UCT 0 20-3

DISPERSANT : WATER
STIRRER : 80 %
PUMP : 80 %
ULTRASONIC : 50 %
ANALYST :

3793 stnd 1HU427M ++ALARMS SET A B C ++

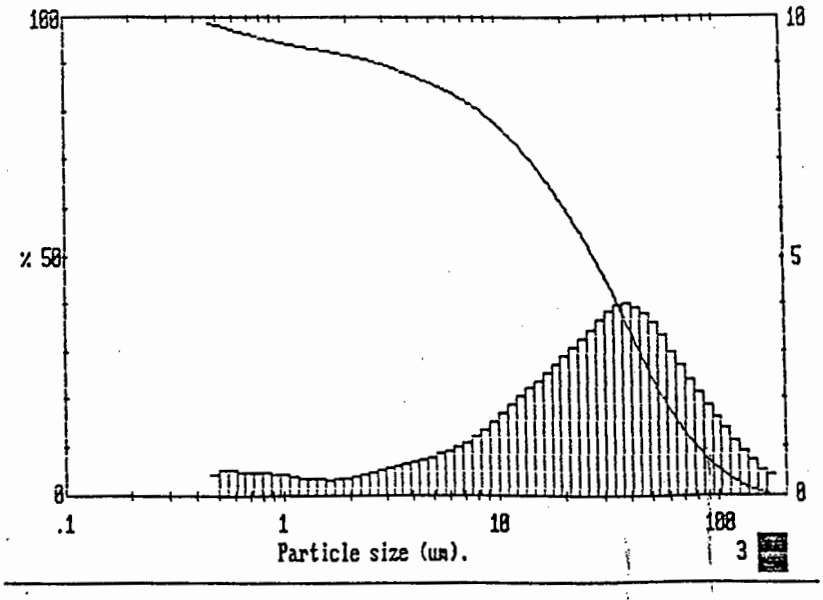
Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.84
				39.1	8.2	32.3	56.5	3.95	1.4	3.27	10.4	
				32.3	7.5	26.7	49.0	3.27	1.1	2.70	9.3	D[4,3] 35.96µm
				26.7	6.7	22.0	42.3	2.70	1.0	2.23	8.3	
				22.0	6.0	18.2	36.3	2.23	0.8	1.84	7.5	
180	1.0	149	99.0	18.2	5.3	15.1	31.1	1.84	0.7	1.52	6.8	D[3,2] 5.68µm
149	1.7	123	97.2	15.1	4.6	12.4	26.5	1.52	0.7	1.26	6.1	
123	2.7	102	94.6	12.4	3.8	10.3	22.7	1.26	0.8	1.04	5.3	D[v,0.9] 80.77µm
102	3.7	83.9	90.9	10.3	3.1	8.48	19.6	1.04	0.9	0.86	4.4	
83.9	4.8	69.3	86.0	8.48	2.5	7.01	17.1	0.86	1.0	0.71	3.5	
69.3	6.0	57.3	80.0	7.01	2.0	5.79	15.0	0.71	1.0	0.59	2.5	D[v,0.1] 3.06µm
57.3	7.3	47.3	72.7	5.79	1.7	4.79	13.3	0.59	1.1	0.48	1.3	
47.3	8.0	39.1	64.7	4.79	1.5	3.95	11.8	0.48	1.3	0.20	0.0	

Source = :Sample
Focal length = 100 mm
Presentation = stnd

Beam length = 2.2 mm
Residual = 0.225 %
Obscuration = 0.1720
Volume distribution

Model indp
Volume Conc. = 0.0213%
Sp.S.A 1.0566 m²/cc.

D[v,0.5] 27.38µm



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:50 pm

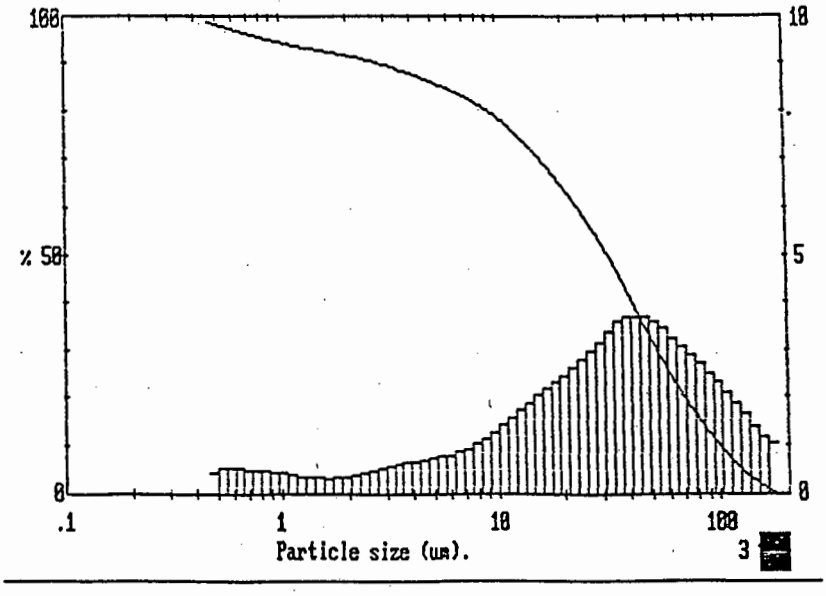
UCT Z RMM082

DISPERSANT : WATER
STIRRER : 80 %
PUMP : 80 %
ULTRASONIC : 50 %
ANALYST :

3793 stnd 1HU427M ++ALARMS SET A B C ++

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 3.05
				39.1	7.4	32.3	50.4	3.95	1.3	3.27	10.6	
				32.3	6.6	26.7	43.8	3.27	1.1	2.70	9.4	D[4,3] 42.66µm
				26.7	5.8	22.0	38.0	2.70	1.0	2.23	8.4	
				22.0	5.1	18.2	32.9	2.23	0.8	1.84	7.7	D[3,2] 5.73µm
180	2.3	149	97.7	18.2	4.5	15.1	28.4	1.84	0.7	1.52	7.0	
149	3.2	123	94.5	15.1	3.9	12.4	24.5	1.52	0.7	1.26	6.3	D[v,0.9] 100.28µm
123	4.2	102	90.3	12.4	3.2	10.3	21.3	1.26	0.8	1.04	5.5	
102	5.0	83.9	85.3	10.3	2.6	8.48	18.7	1.04	0.9	0.86	4.6	
83.9	5.9	69.3	79.4	8.48	2.1	7.01	16.6	0.86	1.0	0.71	3.6	D[v,0.1] 2.98µm
69.3	6.6	57.3	72.8	7.01	1.7	5.79	14.8	0.71	1.0	0.59	2.5	
57.3	7.4	47.3	65.4	5.79	1.6	4.79	13.3	0.59	1.2	0.48	1.4	
47.3	7.6	39.1	57.8	4.79	1.4	3.95	11.9	0.48	1.4	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 31.93µm
	Residual = 0.315 %		
Focal length = 100 mm	Obscuration = 0.3383	Volume Conc. = 0.0478%	
Presentation = stnd	Volume distribution	Sp.S.A 1.0474 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:46 pm

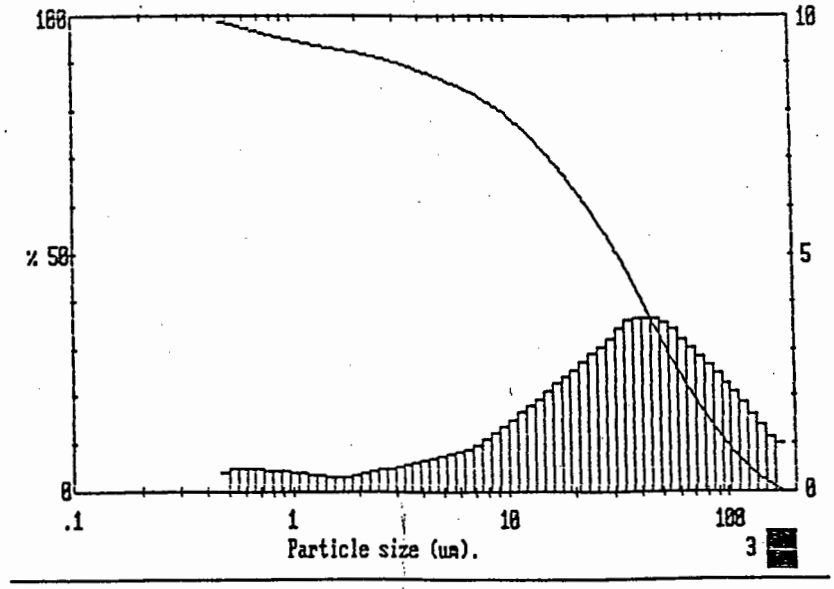
UCT BB RM4090

DISPERSANT	:	WATER
STIRRER	:	80 %
PUMP	:	80 %
ULTRASONIC	:	50 %
ANALYST	:	

3793 stnd 1HU427M **ALARMS SET A B C **

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 3.06
				39.1	7.4	32.3	50.9	3.95	1.3	3.27	10.0	
				32.3	6.6	26.7	44.2	3.27	1.1	2.70	8.9	D[4,3] 42.43µm
				26.7	6.0	22.0	38.3	2.70	0.9	2.23	8.0	
				22.0	5.3	18.2	33.0	2.23	0.8	1.84	7.2	
180	2.3	149	97.7	18.2	4.6	15.1	28.3	1.84	0.7	1.52	6.5	D[3,2] 6.02µm
149	3.2	123	94.6	15.1	4.0	12.4	24.3	1.52	0.7	1.26	5.9	
123	4.1	102	90.4	12.4	3.4	10.3	21.0	1.26	0.8	1.04	5.1	
102	5.0	83.9	85.4	10.3	2.8	8.48	18.2	1.04	0.9	0.86	4.2	D[v,0.9] 99.68µm
83.9	5.8	69.3	79.6	8.48	2.2	7.01	16.0	0.86	0.9	0.71	3.3	
69.3	6.6	57.3	73.1	7.01	1.8	5.79	14.2	0.71	0.9	0.59	2.3	
57.3	7.3	47.3	65.8	5.79	1.6	4.79	12.6	0.59	1.1	0.48	1.2	D[v,0.1] 3.29µm
47.3	7.5	39.1	58.3	4.79	1.4	3.95	11.2	0.48	1.2	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 31.54µm
Focal length = 100 mm	Residual = 0.287 %		
Presentation = stnd	Obscuration = 0.2221	Volume Conc. = 0.0301%	
	Volume distribution	Sp.S.A 0.9959 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:42 pm

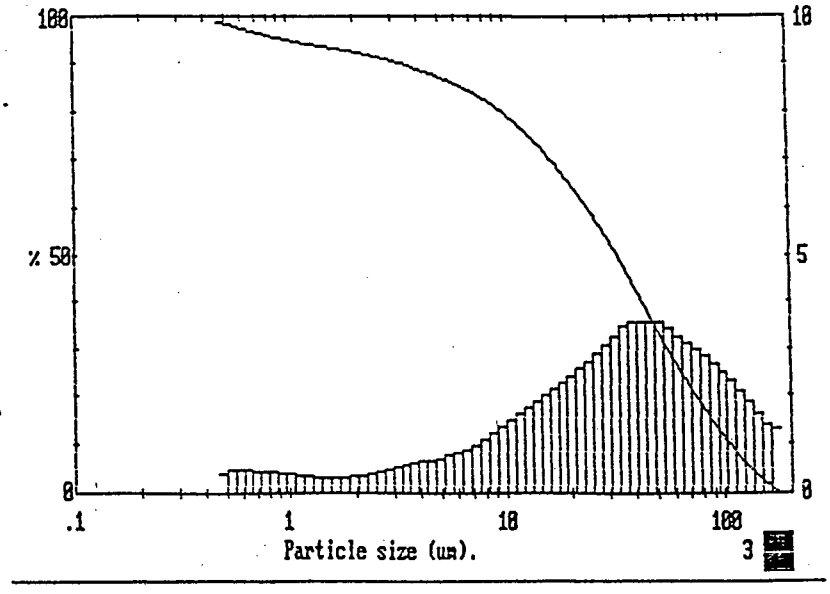
UCT AA RM4089

DISPERSANT	:	WATER
STIRRER	:	80 %
PUMP	:	80 %
ULTRASONIC	:	50 %
ANALYST	:	

3793 stnd 1HU427M **ALARMS SET A B C **

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 3.09
				39.1	7.1	32.3	49.1	3.95	1.2	3.27	9.6	
				32.3	6.3	26.7	42.7	3.27	1.0	2.70	8.5	D[4,3] 44.68µm
				26.7	5.7	22.0	37.1	2.70	0.9	2.23	7.6	
				22.0	5.0	18.2	32.1	2.23	0.7	1.84	6.9	
180	2.8	149	97.2	18.2	4.4	15.1	27.6	1.84	0.6	1.52	6.3	D[3,2] 6.20µm
149	3.7	123	93.5	15.1	3.9	12.4	23.8	1.52	0.6	1.26	5.6	
123	4.6	102	88.9	12.4	3.3	10.3	20.4	1.26	0.7	1.04	4.9	
102	5.4	83.9	83.5	10.3	2.7	8.48	17.7	1.04	0.8	0.86	4.1	D[v,0.9] 105.90µm
83.9	6.1	69.3	77.5	8.48	2.2	7.01	15.5	0.86	0.9	0.71	3.2	
69.3	6.7	57.3	70.8	7.01	1.8	5.79	13.7	0.71	0.9	0.59	2.3	
57.3	7.2	47.3	63.6	5.79	1.6	4.79	12.2	0.59	1.1	0.48	1.2	D[v,0.1] 3.52µm
47.3	7.4	39.1	56.2	4.79	1.4	3.95	10.8	0.48	1.2	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 33.14µm
	Residual = 0.294 %		
Focal length = 100 mm	Obscuration = 0.2570	Volume Conc. = 0.0368%	
Presentation = stnd .	Volume distribution	Sp.S.A 0.9670 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.0A Thu 2 Jul 1992 Time 12:09 pm

UCT V 7-4

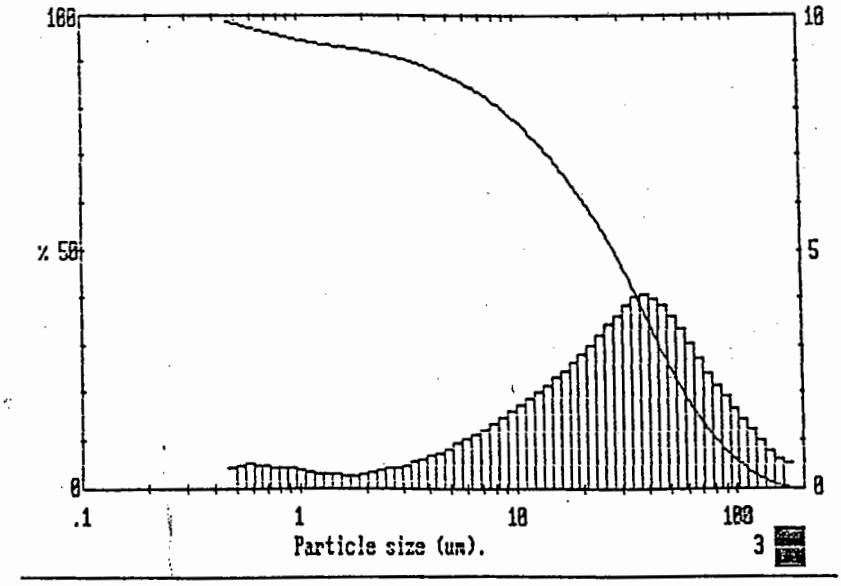
DISPERSANT	: WATER
STIRRER	: 80 %
PUMP	: 80 %
ULTRASONIC	: 50 %
ANALYST	:

3793 stnd 1KU427M ++ALARMS SET A B C ++

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.83
				39.1	8.2	32.3	55.8	3.95	1.2	3.27	9.5	
				32.3	7.5	26.7	48.3	3.27	1.0	2.70	8.5	D[4,3] 36.66µm
				26.7	6.6	22.0	41.7	2.70	0.8	2.23	7.7	
				22.0	5.8	18.2	35.9	2.23	0.7	1.84	7.0	
180	1.2	149	98.8	18.2	5.1	15.1	30.8	1.84	0.6	1.52	6.4	D[3,2] 5.90µm
149	1.9	123	97.0	15.1	4.5	12.4	26.4	1.52	0.6	1.26	5.8	
123	2.8	102	94.2	12.4	3.9	10.3	22.5	1.26	0.7	1.04	5.1	
102	3.8	83.9	90.4	10.3	3.3	8.48	19.2	1.04	0.8	0.86	4.3	D[v,0.9] 82.56µm
83.9	4.8	69.3	85.5	8.48	2.8	7.01	16.4	0.86	0.9	0.71	3.4	
69.3	6.1	57.3	79.4	7.01	2.3	5.79	14.2	0.71	0.9	0.59	2.4	
57.3	7.3	47.3	72.1	5.79	1.9	4.79	12.3	0.59	1.1	0.48	1.3	D[v,0.1] 3.55µm
47.3	8.1	39.1	64.0	4.79	1.5	3.95	10.7	0.48	1.3	0.20	0.0	

Source =	:Sample	Beam length = 2.2 mm	Model indp
		Residual = 0.187 %	
Focal length = 100 mm		Obscuration = 0.2141	Volume Conc. = 0.0284%
Presentation = stnd		Volume distribution	Sp.S.A 1.0165 m²/cc.

D[v,0.5] 27.92µm



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:29 pm

UCT Y 30-3

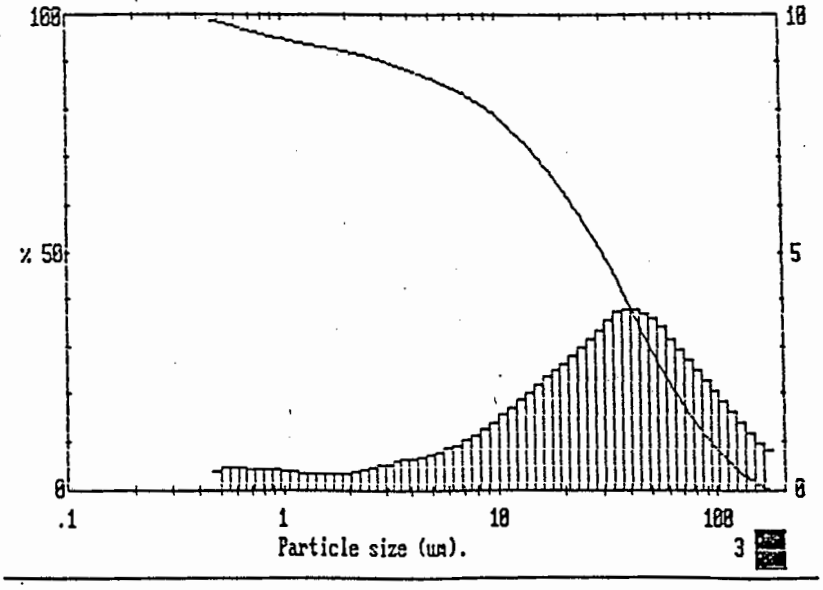
DISPERSANT	:	WATER
STIRRER	:	80 %
PUMP	:	80 %
ULTRASONIC	:	50 %
ANALYST	:	

3793 stnd 1HU427M ++ALARMS SET A B C ++

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 3.01
				39.1	7.7	32.3	52.6	3.95	1.3	3.27	10.0	
				32.3	6.9	26.7	45.6	3.27	1.1	2.70	8.9	D[4,3] 40.41µm
				26.7	6.2	22.0	39.4	2.70	1.0	2.23	8.0	
				22.0	5.5	18.2	34.0	2.23	0.8	1.84	7.2	
180	1.9	149	98.1	18.2	4.8	15.1	28.1	1.84	0.7	1.52	6.5	D[3,2] 6.04µm
149	2.7	123	95.4	15.1	4.2	12.4	25.0	1.52	0.7	1.26	5.8	
123	3.7	102	91.8	12.4	3.5	10.3	21.4	1.26	0.8	1.04	5.0	
102	4.6	83.9	87.2	10.3	2.9	8.48	18.6	1.04	0.9	0.86	4.1	D[v,0.9] 93.93µm
83.9	5.5	69.3	81.7	8.48	2.3	7.01	16.2	0.86	0.9	0.71	3.2	
69.3	6.4	57.3	75.3	7.01	1.9	5.79	14.3	0.71	0.9	0.59	2.3	
57.3	7.3	47.3	68.0	5.79	1.6	4.79	12.7	0.59	1.0	0.48	1.2	D[v,0.1] 3.26µm
47.3	7.7	39.1	60.2	4.79	1.4	3.95	11.3	0.48	1.2	0.20	0.0	

Source = . :Sample	Beam length = 2.2 mm	Model indp
	Residual = 0.245 %	
Focal length = 100 mm	Obscuration = 0.1811	Volume Conc. = 0.0237%
Presentation = stnd	Volume distribution	Sp.S.A 0.9936 m²/cc.

D[v,0.5] 30.16µm



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:26 pm

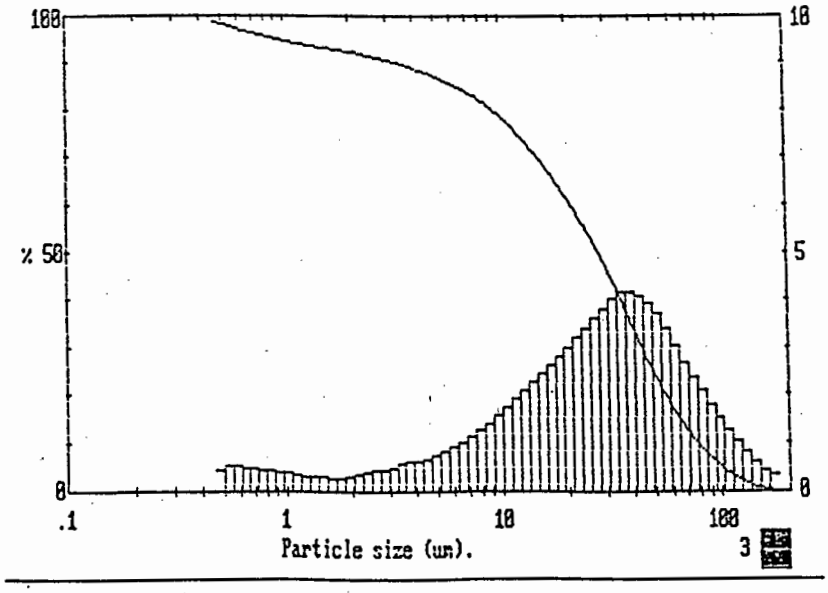
UCT @ 24-3

DISPERSANT : WATER
STIRRER : 80 %
PUMP : 80 %
ULTRASONIC : 50 %
ANALYST :

3793 stnd 1HU427M **ALARMS SET A B C **

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.71
				39.1	8.5	32.3	56.6	3.95	1.2	3.27	9.6	
				32.3	7.8	26.7	48.8	3.27	1.0	2.70	8.6	D[4,3] 35.51µm
				26.7	7.0	22.0	41.8	2.70	0.8	2.23	7.8	
				22.0	6.2	18.2	35.6	2.23	0.7	1.84	7.1	D[3,2] 5.86µm
180	0.9	149	99.1	18.2	5.4	15.1	30.2	1.84	0.6	1.52	6.5	
149	1.5	123	97.6	15.1	4.7	12.4	25.5	1.52	0.6	1.26	5.9	
123	2.5	102	95.2	12.4	3.9	10.3	21.6	1.26	0.7	1.04	5.2	
102	3.5	83.9	91.6	10.3	3.2	8.48	18.3	1.04	0.8	0.86	4.4	D[v,0.9] 78.15µm
83.9	4.7	69.3	86.9	8.48	2.5	7.01	15.8	0.86	0.9	0.71	3.4	
69.3	6.1	57.3	80.8	7.01	2.0	5.79	13.8	0.71	1.0	0.59	2.5	
57.3	7.4	47.3	73.4	5.79	1.6	4.79	12.1	0.59	1.1	0.48	1.3	D[v,0.1] 3.51µm
47.3	8.3	39.1	65.1	4.79	1.4	3.95	10.8	0.48	1.3	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 27.52µm
Focal length = 100 mm	Residual = 0.234 %		
Presentation = stnd.	Obscuration = 0.2376	Volume Conc. = 0.0321%	
	Volume distribution	Sp.S.A 1.0241 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.6A Thu 2 Jul 1992 Time 12:39 PM

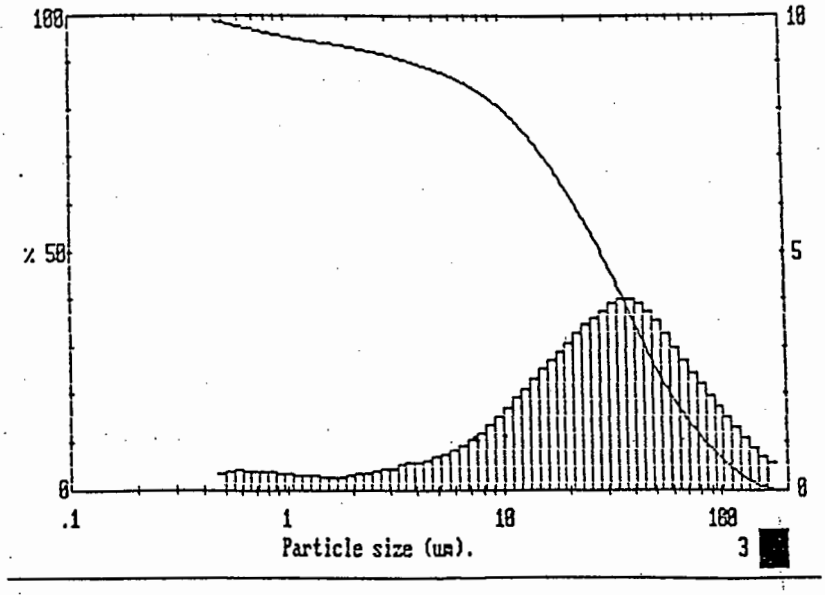
UCT G

DISPERSANT : WATER
STIRRER : 80 %
PUMP : 80 %
ULTRASONIC : 50 %
ANALYST :

3793 stnd 1KU427M ++ALARMS SET A B C ++

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.85
				39.1	8.2	32.3	55.3	3.95	1.1	3.27	8.5	
				32.3	7.7	26.7	47.5	3.27	0.9	2.70	7.6	D[4,3] 37.82µm
				26.7	7.1	22.0	40.4	2.70	0.8	2.23	6.8	
				22.0	6.4	18.2	34.0	2.23	0.7	1.84	6.1	
180	1.3	149	98.7	18.2	5.6	15.1	28.4	1.84	0.6	1.52	5.6	D[3,2] 6.64µm
149	2.1	123	96.6	15.1	4.8	12.4	23.7	1.52	0.6	1.26	5.0	
123	3.0	102	93.6	12.4	3.9	10.3	19.8	1.26	0.6	1.04	4.3	
102	3.9	83.9	89.7	10.3	3.1	8.48	16.7	1.04	0.7	0.86	3.6	D[v,0.9] 85.15µm
83.9	4.9	69.3	84.7	8.48	2.4	7.01	14.3	0.86	0.8	0.71	2.8	
69.3	6.0	57.3	78.7	7.01	1.9	5.79	12.4	0.71	0.8	0.59	2.0	
57.3	7.2	47.3	71.5	5.79	1.5	4.79	10.9	0.59	0.9	0.48	1.1	D[v,0.1] 4.21µm
47.3	8.0	39.1	63.5	4.79	1.3	3.95	9.6	0.48	1.1	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 28.41µm
	Residual = 0.275 %		
Focal length = 100 mm	Obscuration = 0.1583	Volume Conc. = 0.0223%	
Presentation = stnd	Volume distribution	Sp.S.A 0.9035 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:36 pm

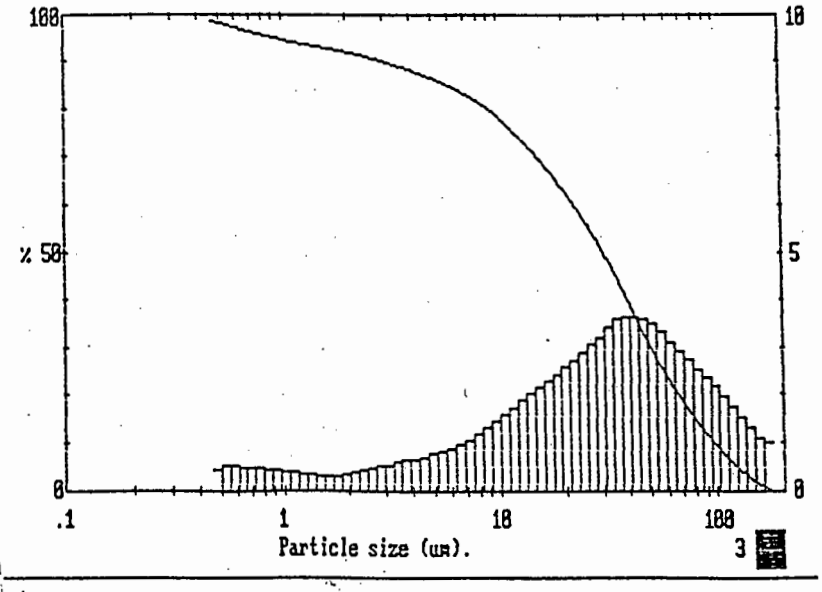
UCT T 27-3

DISPERSANT	: WATER
STIRRER	: 80 %
PUMP	: 80 %
ULTRASONIC	: 50 %
ANALYST	:

3793 stnd 1HU427M ++ALARMS SET A B C ++

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 3.11
				39.1	7.4	32.3	52.2	3.95	1.3	3.27	10.1	
				32.3	6.7	26.7	45.5	3.27	1.1	2.70	9.1	D[4,3] 41.32µm
				26.7	6.0	22.0	39.5	2.70	0.9	2.23	8.1	
				22.0	5.3	18.2	34.2	2.23	0.8	1.84	7.3	D[3,2] 5.85µm
180	2.2	149	97.8	18.2	4.7	15.1	29.5	1.84	0.7	1.52	6.7	
149	3.0	123	94.8	15.1	4.1	12.4	25.4	1.52	0.7	1.26	6.0	
123	3.9	102	90.9	12.4	3.5	10.3	21.8	1.26	0.8	1.04	5.3	D[v,0.9] 97.65µm
102	4.8	83.9	86.2	10.3	2.9	8.48	18.9	1.04	0.9	0.86	4.4	
83.9	5.5	69.3	80.6	8.48	2.4	7.01	16.5	0.86	1.0	0.71	3.4	
69.3	6.4	57.3	74.3	7.01	2.0	5.79	14.6	0.71	1.0	0.59	2.4	D[v,0.1] 3.19µm
57.3	7.2	47.3	67.1	5.79	1.7	4.79	12.9	0.59	1.1	0.48	1.3	
47.3	7.5	39.1	59.6	4.79	1.5	3.95	11.4	0.48	1.3	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 30.40µm
Focal length = 100 mm	Residual = 0.271 %		
Presentation = stnd.	Obscuration = 0.3294	Volume Conc. = 0.0468%	
	Volume distribution	Sp.S.A 1.0262 m²/cc.	



CHEMICAL RESOURCES

MALVERN Instruments SB.8A Thu 2 Jul 1992 Time 12:32 pm

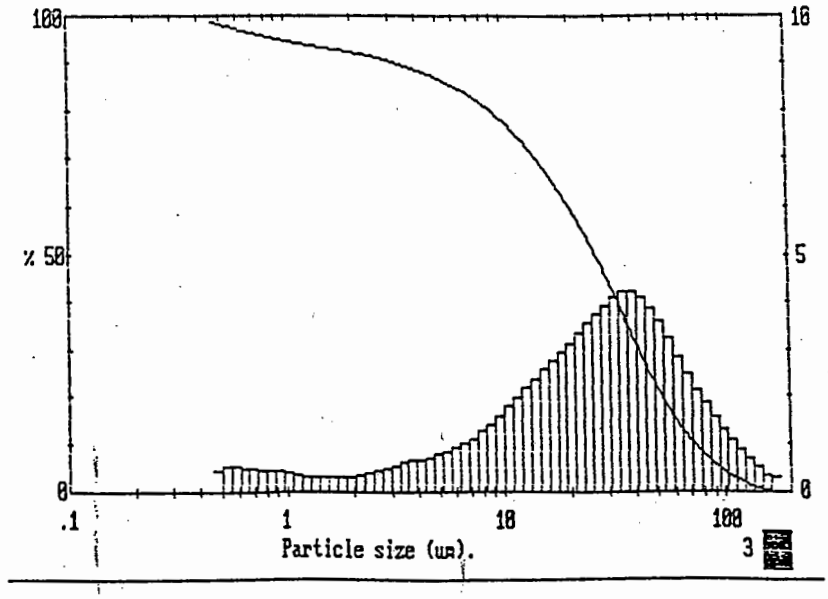
UCT L 17-3

DISPERSANT	: WATER
STIRRER	: 80 %
PUMP	: 80 %
ULTRASONIC	: 50 %
ANALYST	:

3793 stnd 1KU427M **ALARMS SET A B C **

Upper	in	Lower	Under	Upper	in	Lower	Under	Upper	in	Lower	Under	Span 2.66
				39.1	8.7	32.3	58.6	3.95	1.3	3.27	9.9	
				32.3	8.1	26.7	50.5	3.27	1.1	2.70	8.8	D[4,3] 33.77µm
				26.7	7.3	22.0	43.2	2.70	0.9	2.23	7.9	
				22.0	6.5	18.2	36.7	2.23	0.7	1.84	7.2	
180	0.7	149	99.3	18.2	5.7	15.1	31.0	1.84	0.6	1.52	6.6	D[3,2] 5.76µm
149	1.3	123	98.1	15.1	4.9	12.4	26.1	1.52	0.6	1.26	6.0	
123	2.1	102	96.0	12.4	4.1	10.3	22.1	1.26	0.7	1.04	5.2	
102	3.1	83.9	92.9	10.3	3.3	8.48	18.8	1.04	0.8	0.86	4.4	D[v,0.9] 73.31µm
83.9	4.3	69.3	88.6	8.48	2.5	7.01	16.3	0.86	0.9	0.71	3.5	
69.3	5.7	57.3	82.9	7.01	2.0	5.79	14.3	0.71	1.0	0.59	2.5	
57.3	7.3	47.3	75.6	5.79	1.7	4.79	12.6	0.59	1.1	0.48	1.3	D[v,0.1] 3.34µm
47.3	8.3	39.1	67.3	4.79	1.5	3.95	11.1	0.48	1.3	0.20	0.0	

Source = :Sample	Beam length = 2.2 mm	Model indp	D[v,0.5] 26.33µm
	Residual = 0.251 %		
Focal length = 100 mm	Obscuration = 0.2274	Volume Conc. = 0.0298%	
Presentation = stnd	Volume distribution	Sp.S.A 1.0414 m²/cc.	



CHEMICAL RESOURCES

APPENDIX 11

SAND GRADING

Sieve Size (μm)	Percentage Passing	
	SABS 1083	Suggested Outer Limits
4 750	90 - 100	85 - 100
2 360	-	60 - 100
1 180	-	40 - 100
600	-	30 - 75
300	-	15 - 45
150	0 - 15	5 - 20
75	0 - 5	0 - 12